Chloride waters of Great Britain revisited: from subsea formation waters to onshore geothermal fluids

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A B S T R A C T

It has long been known that chloride-dominated saline ground waters occur at depth in the UK, not only beneath the sea but also onshore at depths of a few hundred metres. In a few places in northern England, these saline waters discharge naturally at surface in the form of springs. In recent years, however, these saline ground waters have come to be regarded as resources: as potential geothermal fluids intercepted in deep boreholes. Comparisons of the major ions and stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{34}S$) of these saline ground waters with North Sea oilfield formation waters, and with brines encountered in former subsea workings of coastal collieries, reveal that they are quite distinct from those found in North Sea oilfields, in that their as $\delta^2H/\delta^{18}O$ signatures are distinctly "meteoric". $\delta^{34}S$ data preclude a significant input from evaporite dissolution – another contrast with many North Sea brines and some colliery waters. Yet, enigmatically, their total dissolved solids contents are far higher than typical meteoric waters. It is tentatively suggested that these paradoxical hydrogeochemical properties might be explained by recharge during Cenozoic uplift episodes, with high concentrations of solutes being derived by a combination of high-temperature rock–water interaction in the radiothermal granites and/or 'freeze out' from overlying permafrost that surely formed in this region during cold periods. Geothermometric calculations suggest these saline waters may well be representative of potentially valuable geothermal reservoirs.

1. Introduction

Saline ground waters have long been an object of fascination in the UK. Some saline springs were venerated in antiquity (Robins and Smedley, 2013), but they only entered the era of scientific research in the mid-19th Century when issues arose with such waters in coal mines (e.g. Armstrong, 1856; Dunn, 1877; Clowes, 1889). The first attempted synthesis on the occurrence and geological significance of saline waters in the UK was the paper of Anderson (1945) "On the chloride waters of Great Britain". Notwithstanding the nationwide scope of the title, this paper focused mainly on saline waters in the Great Northern Coalfield of England, for the simple reason that more chemical investigations had been undertaken on saline waters there than elsewhere (e.g. Clowes, 1889). Anderson (1945) investigated Na-(Ca)-Cl springs and mine waters, and offered some early suggestions as to possible origins of these waters. However, there were insufficient data

available at the time to support a comparative assessment of the affinities of the different saline ground waters, and isotope hydrogeochemistry had not then been pioneered. All of this began to change as deep mining proceeded beneath the North Sea, encountering prolific brines, and as the North Sea oil and gas fields were opened up.

It is in the same part of the UK where Anderson (1945) worked that renewed interest in onshore saline waters has recently arisen, also in relation to the energy sector, though in this case it is geothermal energy, rather than fossil fuels, that is of interest (Younger et al., 2012). There are two types of target reservoir (Downing and Gray, 1986): radiothermal granites (e.g. Manning et al., 2007; Younger and Manning, 2010), in which heat is produced by spontaneous decay of radioisotopes of uranium, thorium and potassium (see McCay et al., 2014); and deep sedimentary aquifers, such as the Fell Sandstones of Northumberland (Craddock-Hartopp and Holliday, 1984; Younger, 2013). Nevertheless, this sunrise energy industry can learn much of value from its fossil-based predecessors: from studies of saline mine waters and from comparisons with oilfield brines found beneath the North Sea. This paper examines what the lessons might be,

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using a mixture of pre-existing hydrochemical analyses and new isotopic measurements, interpreted in a broad geological framework.

2. Saline waters of the UK: offshore and onshore

2.1. Natural systems

The UK can boast only a modest catalogue of natural saline springs, some of which are attested in antiquity and still flow strongly today (e.g. Feather, 1966; Andrews and Kay, 1983; Edmunds et al., 1998), whole others are no longer flowing, yet their former presence is echoed in place-names (such as Saltwell in Gateshead; Anderson, 1945; Banks et al., 1996). These naturally saline springs were sometimes lauded for supposed health-promoting properties, albeit such claims do not stand up to scientific scrutiny (Robins and Smedley, 2013).

In practice, the key issue surrounding salinity and public water supplies is the risk of salinisation rendering freshwaters undrinkable. Saline ground waters are widely reported at depth beneath the freshwater bodies in major UK aquifers such as the Chalk (e.g. Lloyd et al., 1978) and the Permo-Triassic sandstones (e.g. Tellam and Lloyd, 1986; Tellam, 1995; Bottrell et al., 2006). In such settings, saline ground waters have a marked propensity to "upcone" (Chandler and McWhorter, 1975) or migrate up-dip (Bottrell et al., 2006) into the freshwater portions of the aquifers in response to strong hydraulic gradients imposed by pumping of wells. Such upconing behaviour is closely analogous to the intrusion of saline, marine groundwater into coastal aquifers, from which it can at times be difficult to distinguish unequivocally (e.g. Howard and Lloyd, 1983; Tellam and Lloyd, 1986). Beyond the major aquifers, saline ground waters have also been reported from a range of other geological settings in the UK, some of them associated with anomalously high ground water temperatures (e.g. Andrews and Kay, 1983; Edmunds, 1984; Manning and Strutt, 1990; Manning et al., 2007), others with unexceptional temperatures (e.g. Hamilton-Taylor et al., 1988; Bath et al., 1996; Bottrell et al., 1996; Darling et al., 1997; Edmunds et al., 1998). Salinity sources deduced for briny groundwaters in the UK range from intrusion of modern sea water (e.g. at West Hartlepool; Younger, 1995a) through ongoing dissolution of evaporite minerals such as

halite (Bottrell et al., 1996, 2006) to upconing of very deep, old saline waters of enigmatic or complex origins (e.g. Edmunds, 1984; Bath et al., 1996).

2.2. Saline mine waters

Sea water intrusion, evaporite dissolution and/or upconing of very old saline waters have all been invoked to varying degrees to explain the brines that have frequently been encountered in the deeper UK coal mines (e.g. Armstrong, 1856; Anderson, 1945; Edmunds, 1975; Banks et al., 1996; Younger, 1998). In the case of subsea collieries, ingress of saline waters naturally gave rise to concern, lest they should prove to be modern sea-water, in which case there would have been an existential threat not only to the continuation of coal mining but (should a trickle become an inrush) to the lives of the miners themselves. Every new occurrence of saline water in the subsea collieries was therefore subjected to stringent and rapid sampling and chemical analysis. It is a matter of considerable pride to those involved in subsea mining that in more than a hundred years of longwall working beneath the ocean, modern sea water was never once detected in deep subsea workings (Younger, 2004). Sea water did, of course, invade some old, shallow workings that were developed before the science of rock mechanics had advanced to the point where mines could be designed to avoid dangerous inrushes of water. The most extreme case occurred in July 1837, when a veritable whirlpool formed in Workington harbour following roof collapse in a mine only 45 m below the seabed, following removal of a coal pillar; the ensuing seawater inrush killed 27 miners (Galloway, 1904). More recently, Elliot and Younger (2007) reported a marine component in waters pumped from the flooded workings of the Frances Colliery in Fife (though again this was attributed to passage via shallow old workings, *not* the modern subsea longwall workings). Less dramatically, brines encountered in coal mines posed problems of scale accumulation (e.g. Dunn, 1877) and/or corrosion to dewatering pumps and pipes. In some instances they gave rise to voluminous evaporite precipitates that were sufficiently voluminous that they could hinder ventilation (Fig. 1). Coal mine brines often remained a nuisance after they had been pumped to surface: disposal to soakaway basins led to extensive and persistent pollution of the chalk aquifer in Kent, for instance
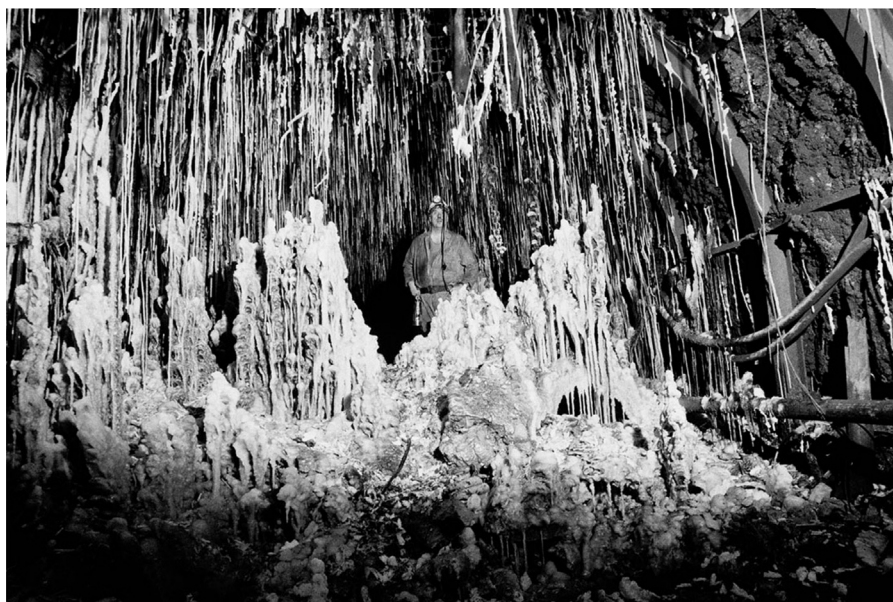

Fig. 1. Halite speleothems, precipitated by evaporation of saline mine waters, partially blocking a roadway used for ventilation purposes in Westoe Colliery (South Shields, Tyne and Wear, UK) in the early 1990s. (Photograph courtesy of Dr. Aidan Doyle).

(e.g. Headworth et al., 1980; Watson et al., 2012), while rivers in the English Midlands were markedly salinized in places due to receipt of mine waters (Lemon, 1991).

The occurrence of saline water in mines has long sparked the curiosity of geoscientists investigating the mineralisation of UK orefields, such as the Cornubian Province (Edmunds, 1984) and the North Pennine Orefield (Sheppard and Langley, 1984; Dunham, 1990; Manning and Strutt, 1990; Cann and Banks, 2001). Given that many base metals are distinctly mobile in more saline waters, one common concept for ore formation is that mixing of metalliferous brines with ground waters of lower ionic strength could explain the localisation of mineral deposits in veins that occupy the planes of faults and similar rock–mass discontinuities, which were evidently permeable prior to ore genesis (e.g. Dunham, 1990). This concept was dramatically illustrated by the formation of barite scales in pipe ranges carrying mixtures of shallow- and deep-sourced mine waters out of collieries in north-east England (Dunn, 1877; Clowes, 1889); hence there is no doubt of the viability and rapid kinetics of the process. Nevertheless, the precise role of brines as mineralising fluids in natural systems is far from being fully elucidated. A key element of uncertainty is the ultimate origin of the metalliferous brines: are they modified seawater, remnants of dissolution of Permian halite, deep basinal fluids that have seen their dissolved solids load increased by "membrane filtration" across mudstone units (with high driving heads forcing much of the water across the mudstone while the solutes remain trapped on the up-gradient side), or some mix of these (and other) processes? Halogen analyses is beginning to elucidate the origins of the latter, with, for example, evaporated Lower Carboniferous seawater strongly implicated as the primary brine in hydrothermal fluids forming the intensely mineralised Irish Zn+Pb ore field (Banks et al., 2002).

2.3. Saline waters from hydrocarbon reservoirs

Saline waters are commonplace in oil- and gas-fields worldwide, where they dominate the 'co-produced' or 'formation' waters that are inevitably pumped to surface during sustained hydrocarbon production (e.g. Richter and Kreitler, 1991). The UK's largest onshore oilfield (Wytch Farm, Dorset) hosts Na-Cl brines with up to 230,000 ppm total dissolved solids (TDS), which to judge from Br/Cl ratios were derived by dissolution of nearby evaporites of Triassic age in a number of episodes of meteoric water circulation prior to about 40 Ma (Worden et al., 2006). In the North Sea, brines range in TDS from 20,000 to 300,000 ppm (Bjørlykke and Gran, 1994) and are overwhelmingly of Na-Cl facies (Warren and Smalley, 1993, 1994).

Lateral and vertical spatial variations in TDS, and subtle variations in proportions of auxiliary cations (especially K and Mg), reflect the complexities of basin evolution (McCartney et al., 2004). For instance, in the Brent Formation, variations in major ion and isotope signatures have been interpreted in terms of ingress of meteoric waters during uplift and erosion in the late Jurassic/early Cretaceous, which partly displaced the marine waters that had been present in the strata since deposition, followed by ingress of Na-Cl waters derived from dissolution of Permo-Triassic evaporites and renewed invasion by evapo-concentrated marine waters during subsequent down-warping of the Viking Graben (Ziegler et al., 2001). The interaction of such processes in time and space has resulted in marked stratification of salinity in many North Sea reservoirs. For instance, Bjørlykke and Gran (1994) note that a tendency towards increased salinity with depth is most marked where evaporites are present in the sequence (e.g. in the southern North Sea), but that high salinity pore waters (>100,000 ppm) are found only at depths in excess of 2200 m. This observation is interpreted by Bjørlykke and Gran (1994) as precluding invocation of large-scale convection of pore water during diagenesis. Unravelling the chemical evolution of these

formation waters is not only useful for enhancing understanding (and thus production) of associated oil and gas resources (Bjørlykke and Gran, 1994; Ziegler et al., 2001), but it also offers valuable insights that can be harnessed for monitoring the effectiveness of particular production strategies, such as water-flooding (e.g. Munz et al., 2010).

3. Methods

3.1. Data sources and hydrochemical facies determination

This paper reports new analyses for saline waters obtained from boreholes in Gateshead and Newcastle, as well as new isotope data for the saline waters accessed by the Eastgate No 1 geothermal borehole in Weardale (County Durham). Analytical methods are summarised below (Sections 2.2 and 2.3).

Using the classification techniques first introduced by Back (1960, 1962), we have determined the hydrochemical facies of these saline waters (and of other saline waters previously analysed by others, notably: Sheppard and Langley, 1984; Edmunds, 1975; Manning et al., 2007; Cooper, 2011). Hydrochemical facies comprise identification of the predominant cations and anions in a given water, when these are compared on an "equivalents" basis, i.e. by converting the ppm concentrations into milliequivalents per litre and examining which then dominate the total of all the dissolved cations and anions. Often just one cation and anion (e.g. Na-Cl, or Ca-HCO$_3$) will adequately describe the facies (Back, 1961); in other cases, where a second ion of either charge accounts for a significant proportion of the solute load, an auxiliary cation or anion may be listed in parentheses. The identification of hydrochemical facies is a useful first step in mapping spatial and temporal patterns in hydrogeochemistry (Younger, 2007), and relating these to processes such as rock–water interaction along groundwater flow paths. For instance, in a study of the ground waters of the Vale of Eden, Cumbria (Younger and Milne, 1997), it was found that shallow, recently recharged groundwaters were predominantly of Ca-HCO$_3$ facies – reflecting open system calcite dissolution – except in areas where Permian gypsum occurs, where the predominant facies was Ca-SO$_4$. In the case of brines, monotonous Na-Cl facies might well be anticipated, but where subtle variations in secondary ions occur, these can be quite suggestive of geological processes (e.g. Richter and Kreitler, 1991).

3.2. Physico-chemical parameters and solutes

pH, temperature, specific electrical conductance ('conductivity') and total dissolved solids (automatically calculated from conductivity using the relationship TDS (ppm) = 0.65 × conduc-conductivity (μS/cm)) were all measured in the field using a hand-held instrument (Myron P Ultrameter), which was calibrated before each day's fieldwork. Alkalinity was also determined in the field with a HACH handheld digital titrator, using nitric acid and a bromcresol green – methyl red indicator (pH). Major anions and or cations and anions reported in this paper were analysed in the laboratories of the School of Civil Engineering and Geosciences at Newcastle University according to the Standard Methods of the US Public Health Laboratories. Cation analysis was by ICP-MS while anions were determined using ion chromatography.

3.3. Stable isotopes

The isotope analyses were undertaken at the SUERC laboratories, East Kilbride. For H isotope analysis, sample and standard waters were directly injected into a chromium furnace at 800 °C (Donnelly et al., 2001), with the evolved H$_2$ gas analysed on-line on a VG Optima mass spectrometer. Replicate analyses of water
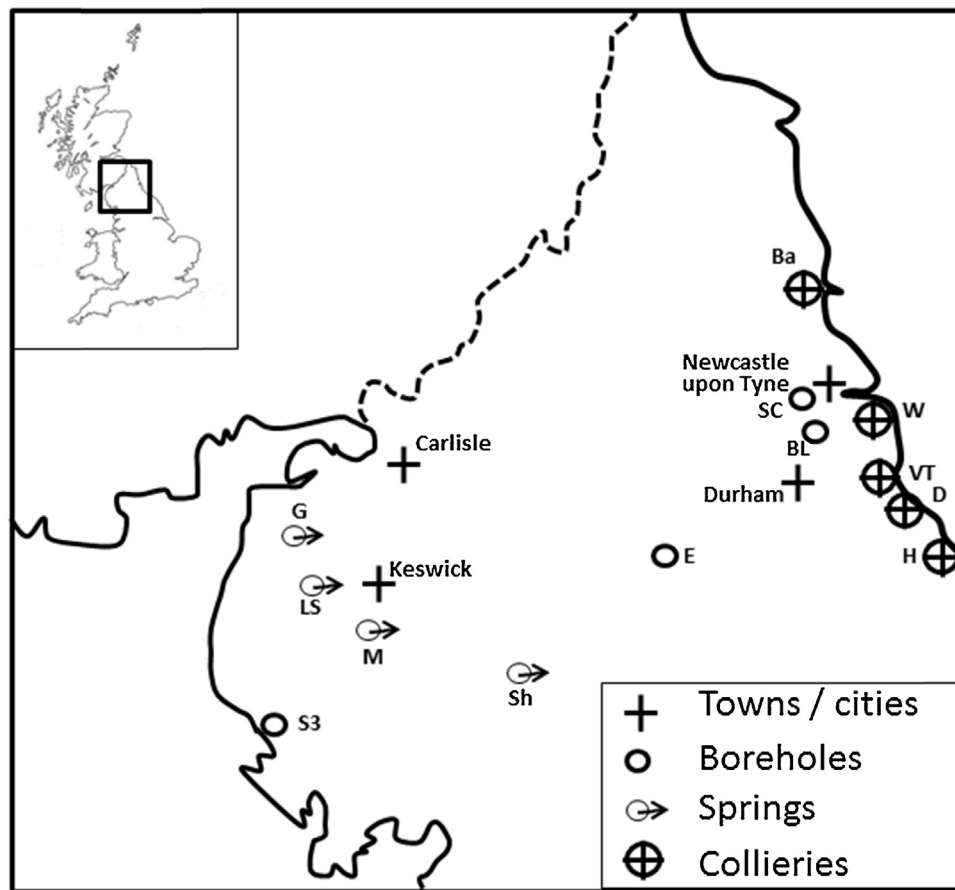
Fig. 2. Sketch map of northern England showing the locations mentioned in the text and in Tables 1–4. Ba, Bates Colliery; BL, Bassett's Lookout borehole; D, Dawdon Colliery; E, Eastgate Boreholes (1 and 2); G, Gilcrux spring; H, Horden Colliery; LS, Lorton Stanger spring; M, Manesty spring; S3, Sellafield Borehole no 3; SC, Science Central Borehole; Sh, Shap Spa spring; VT, Vane Tempest Colliery; W, Westoe Colliery.

standards (international standards V-SMOW and GISP, and internal standard Lt Std gave a reproducibility of ±3‰. For O isotope analysis of water, 200 μl of the water samples analysed by standard techniques on a Thermo Scientific Delta V mass spectrometer, set at 25 °C. Each sample was over-gassed with a 1% CO_2-in-He mixture for 5mins and left to equilibrate for a further 24 h before mass spectrometric analysis. O data were then produced using the method established by Nelson (2000). As with H isotopes, data are reported as per mille variations from the V-SMOW standard. During the analyses of these samples, reproducibility of the data, based on within-run repeat analyses of V-SMOW, GISP and Lt Std, was around ±0.3‰. Isotopes of sulfur in sulfate were performed by precipitating dissolved sulfate as barium sulfate, then using the technique of Coleman and Moore (1978), in which SO_2 gas is liberated by combustion at 1125 °C with excess Cu_2O and silica before analysis on a VG Isotech SIRA II mass spectrometer. Resulting values have 1σ reproducibility better than ±0.2‰, and are reported in $\delta^{34}S$ notation as per mil (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard. The sulfate-oxygen analysis procedure is detailed in Hall et al. (1991). Reproducibility of the technique based on repeat analyses of the NBS-127 standard was around ± 0.3‰, reported as per mil (‰) variations versus V-SMOW.

4. Hydrogeochemistry of geothermal waters in northern England

A recent summary of the history of geothermal investigations throughout the UK has been given by Younger et al. (2012). There are no substantive updates to add to that account at the time of writing, inasmuch as the only boreholes that have been drilled for

geothermal exploration anywhere in the UK in the 20th Century remain the three listed by Younger et al. (2012), which were all drilled under the direction of the first and third authors of the present paper, at two sites in northern England (Fig. 2):

- The *Eastgate Geothermal Exploration Boreholes* (Weardale, County Durham), where the radiothermal Weardale Granite was encountered some 270–280 m below ground in two separate boreholes: Eastgate No 1 (UK National Grid reference NY 9389 5382), which was completed to a depth of 995 m in 2004 (Manning et al., 2007), and Eastgate No 2 (NY 94526 38126) which was completed to 420 m in 2010. Both boreholes penetrated a sedimentary cover sequence comprising inter-bedded limestones, mudstones and thin sandstones of Lower Carboniferous age, within which a regionally extensive dolerite intrusion, the Great Whin Sill, was found in the depth intervals 91–157.5 m (Eastgate No 1) and 109–167.5 m (Eastgate No 2). Both boreholes encountered highly saline groundwater, though only Eastgate No 1 intersected a highly permeable regional-scale strike-slip fault (the Slitt Vein), which yielded abundant water during test-pumping in 2006 (Younger and Manning, 2010) and in 2010 (Younger et al., 2012).
- *Science Central Geothermal Exploration Borehole*, Newcastle upon Tyne (NZ 2401 6433), which was drilled to a total depth of 1823 m in 2011. This borehole targeted a deep sedimentary aquifer (the Fell Sandstones; see Turner et al., 1993), which in this location could be hydraulically connected to the Weardale Granite heat source some 8 km distant by a regional extensional fault zone (the Ninety Fathom – Stublick Fault). The Fell Sandstones were indeed encountered, comprising some 300 m

Table 1
Summary of hydrochemistry of saline waters encountered in three boreholes in north-east England: Eastgate No 1 (NY 9389 5382), Science Central (NZ 2401 6433) and Bassett's Lookout (NZ 2802 5700). Unless otherwise stated, concentrations are in ppm (=mg/kg). n.d., not determined.

Borehole	Eastgate No 1	Science Central	Bassett's Lookout
Date of sample	10th March 2006	7th July 2011	30th Nov 2004
Depth of sample	411 m	1560 m	170 m
Temp. (°C)	27	38.5	12
pH	6.7	11.7	6.85
Total dissolved solids (TDS)	43,017	5819	13,325
Ca	6070	37.3	382
Mg	69.8	<0.1	307
Na	9630	1166	4690
K	720	110	91
SO_4	26	310	6260
HCO_3	67.2	1435	1032
Cl	29,280	966	4360
δ^2H (of water)	-53.4 ± 0.5	n.d.	n.d.
$\delta^{18}O$ (of water)	-8.7 ± 0.06	n.d.	n.d.
$\delta^{18}O$ (of sulfate)	-3.9 ± 0.3	n.d.	n.d.
$\delta^{34}S$ (of sulfate)	3.3 ± 0.3	n.d.	n.d.
Facies	Na-Ca-Cl	Na-Cl-HCO_3	Na-(Ca,Mg)-SO_4-Cl

of fine- and medium-grained sandstones in the depth interval from around 1500–1800 m. The sandstones were underlain by a sequence of thinly inter-bedded mudstones, sandstones and anhydrite of the Ballagan Formation (lowermost Carboniferous). Water collected from the drill rig separators during drilling was sampled and analysed on several occasions.

A third borehole drilled in the same region unexpectedly encountered saline ground water, and is reported here for the first time:

- The *Bassett's Lookout Borehole* (NZ 2802 5700), Birtley (Tyne and Wear; Fig. 2), was drilled in the Autumn of 2004 to a total depth of 210 m, in a search of fresh groundwater to help top-up adjoining fish ponds (which had just been constructed but were as yet empty). Fresh water was indeed encountered in fractured sandstones between 24 m and 39.7 m depth, but on test-pumping this source of water was rapidly depleted, indicating a perched aquifer of limited lateral extent. The borehole was therefore continued in stages to total depth, encountering five horizons of old coal mineworkings en route (at approximately 70 m, 100 m, 115 m, 135 m, and 173 m), which had to be cased-off from the borehole to restore drilling fluid circulation. The uppermost four sets of old mineworkings were all dry, presumably due to the sustained mine water pumping by the Coal Authority at the nearby Kibblesworth Shaft (NZ 2433 5622; Younger, 1998), the collar of which lies at 75 m AOD (compared to 110 m AOD at Bassetts Lookout). Below the deepest mine workings, however, the driller could tell from his air pressure gauge that the bit had again encountered water, and although there was very little return of flush or cuttings (they were presumably retained in the mineworkings at around 173 m), brief flushes of water were sometimes air-lifted to surface. The driller reported these as being 'warmer than usual'. After drilling ceased, a rest water level 169.14 m below ground (i.e. about 59 m below sea level) was measured using a standard electrical contact probe. A reliable sample of this deep water was obtained on 30th November 2004 during final reaming works. Since the water proved far too saline for the owners' purposes, the borehole was later backfilled with pea gravel and sealed with bentonite above the shallowest mineworkings (i.e. at 65 m), so that the borehole is no longer open to the deep saline water source.

Table 1 summarises the major ion chemistry of the saline waters found in Eastgate No 1, Science Central and Bassett's Lookout, together with isotope data for Eastgate No 1. It should be noted that the 'depth of sample' in each case is an estimate based on the contemporaneous hydrogeological conditions, which differed in all three cases. At Eastgate No 1, packer-testing (Younger and Manning, 2010) demonstrated that the water produced from the borehole was dominated by a single inflow at 411 m depth. At Science Central, the borehole had been cased-off to 1000 m, and low-permeability mudstones had dominated the sequence between the toe of the casing and the Fell Sandstones, so that the depth of drilling at the time the sample was collected could be taken as representative of the sample depth. At Bassett's Lookout, the sample was obtained by air-lifting from the depth indicated, from a static water column that rested only a few metres above the water intake to the pipework.

While pH was measured in all three cases, in the case of Science Central the measured value was strongly suspected to be affected by drilling additives, so the reported value for that water is believed to be artificially elevated. Otherwise, it is clear that the waters are of near-neutral pH. In terms of hydrochemical facies, sodium is the dominant cation and chloride the dominant anion in all three, though calcium is a significant auxiliary cation in Eastgate No 1 and Bassett's Lookout, with magnesium also being important at the latter. As regards auxiliary anions, HCO_3^- is notable in Science Central, and SO_4^{2-} in Bassett's Lookout.

5. Discussion

5.1. Mining and the lost saline springs of north-east England

"...Formerly there were several surface brine springs in the North-East Coalfield; to-day there are none ... Underground brine springs have been encountered during mining operations in the North-East Coalfield for more than a century ..." (Anderson, 1945).

The observation of sodium chloride waters in northern England is clearly nothing new. It has long been supposed that the disappearance of former surface brine springs documented by Anderson (1945) is down to the progressive dewatering and fracturing of the Coal Measures over the three hundred years of deep mining (e.g. Banks et al., 1996). As the "permeabilisation" of the subsurface wrought by mining presumably allowed enhanced infiltration and circulation of meteoric water – i.e. water derived from the atmosphere as precipitation – the original brines were only likely to be found at ever-greater depths, and even then to be diluted to some degree by incoming fresh water. Since the early 1990s, much work has been done on the hydrogeology of mined

Table 2

Summary of key parameters of saline waters previously encountered in, and currently pumped from, undersea coal mine workings in northern England. For locations see Fig. 2. All values in ppm with the exception of pH and isotopic data. Raw data from Sheppard and Langley (1984), except for the three samples labelled 'pumped', with a sampling date in parentheses, which are courtesy of the Coal Authority. The depth of the sample relative to OD is given for waters sampled underground. The 'pumped' samples were all collected at surface, but are representative of water pumped from a mixture of underground sources converging on the pumping shaft. For these samples, TDS is calculated from conductivity and HCO$_3$ from total alkalinity (multiplication by 1.2). Hydrochemical facies identifications by the present authors.

Colliery	Horden (−237 m OD)	Dawdon (−442 m OD)	Vane Tempest (−530 m OD)	Westoe (−229 m OD)	Horden pumped 30th Oct 2013	Dawdon pumped 21st Nov 2012	Bates pumped 12th Nov 2012
Grid ref	NZ 4772 4383	NZ 4435 5478	NZ 4550 5162	NZ 4426 5700	NZ 440 421	NZ 435 478	NZ 305 823
pH	6.4	7.2	6.1	6.5	6.5	7.5	7.4
TDS	115,160	60,540	197,000	114,400	28,470	43,940	9425
Ca	6286	3724	16,176	1522	919	1130	398
Mg	1482	705	2673	2772	570	690	436
Na	36,150	18,650	54,434	38,800	9200	13,800	2010
SO$_4$	107	300	<1	3500	2540	3040	2870
HCO$_3$	n.d.	n.d.	n.d.	n.d.	335	469	959
Cl	71,100	37,000	122,000	67,800	12,600	21,900	2530
δ^2H (of water)	−51.4	−63.0	−36.7	−62.2	n.d.	n.d.	n.d.
δ^{18}O (of water)	−7.2	−7.2	−4.9	−8.8	n.d.	n.d.	n.d.
Facies:	Na-Cl	Na-Cl	Na-(Ca)-Cl	Na-Cl-(SO$_4$)	Na-Cl	Na-Cl	

Coal Measures in this region (Younger, 1993a, 1995b, 1998), and this largely vindicated the above presumption: most of the waters flowing out of abandoned underground coal workings in the region are of modest mineralisation (TDS ≤ 1000 mg/L), with hydrochemical facies that correspond to those of typical fresh groundwaters (i.e. Ca-HCO$_3$) with additional iron and sulfate reflecting oxidative dissolution of pyrite above the water table (Younger, 1995b). Yet, as we have seen, highly saline waters continued to be encountered at depth in working coal mines (Edmunds, 1975; Sheppard and Langley, 1984) and a notable saline component has long been evident in those mine waters pumped from significant depth at several old shafts now used as pumping stations (e.g. Younger, 1998). It had long been supposed that the saline component was drawn from substantial depths, so that recovery of water levels in the workings as pumping was reduced or terminated would be accompanied by a marked "freshening-up" of water quality. It is in this context that the discovery of very saline, sodium-chloride water at a depth of only 170 m in the Bassett's Lookout borehole (Table 1) came as something of a surprise. Although this water does have a noticeable auxiliary sulfate component, diagnostic of some interaction of infiltrating waters with pyrite in an oxidising atmosphere, the overall facies of the water is undoubtedly saline. The Bassett's Lookout borehole is located about midway between two of the former surface brine springs noted by Anderson (1945), i.e. Saltwell in Gateshead and the Birtley Springs. (Although Anderson (1945) claimed that the precise locations of these had been forgotten, there is a conspicuous spring head memorial stone above a dry fount at Saltwell (NZ 2527 6102), and a street in Birtley called The Springs (NZ 2799 5510) is attested by local families as being located right where the former salt springs once flowed). The ground surface at the three locations is as follows: Saltwell 42 m AOD; Bassett's Lookout 110 m AOD; Birtley Springs 65 m AOD. If the water encountered at 170 m depth in Bassett's Lookout is from the same source as these two former springs, then given that this source now has a hydraulic head some 60 m below OD, the head is 125 m below the former outflow point at Birtley, and 102 m below that at Saltwell. This is consistent with the notion that mining and mine dewatering are responsible for the disappearance of former surface brine springs in this region.

Elsewhere in the region, coal mine waters are still pumped by the Coal Authority for environmental protection purposes. As mentioned previously, the nearest pumping station to Bassett's Lookout is Kibblesworth (NZ 2433 5622), located just 3.5 km to the west-southwest, which pumps brackish mine water (TDS ≈ 2800 ppm) of Na-Cl facies (Younger, 1998). Water levels in the Kibblesworth pumping shaft have gradually risen over the last 17 years in response to changing pumping patterns, from

about −70 m OD in 1997 to −25 m OD in 2004, when the Bassett's Lookout borehole was sampled. Already at that time, then, the hydraulic heads were such that the saline waters encountered at Bassett's Lookout cannot have been draining west to Kibblesworth, but must have been reflecting greater drawdowns to the east, towards the coast. The Coal Authority currently operates three major coastal pumping stations: Bates, Dawdon and Horden (see Fig. 2 and Table 2). At the latter two sites, samples of saline waters had also been collected previously by Edmunds (1975) and Sheppard and Langley (1984). Data from the latter source are included in Table 2, along with recent analyses of the pumped waters from the three Coal Authority pumping stations. The salinities of the pumped waters (last three columns in Table 2) are substantially lower than those previously reported from the earlier, discrete subsurface samples in these same collieries (first two columns of Table 2); this is consistent with an element of dilution by less saline waters coming from onshore sources. Nevertheless, all of the pumped waters are of Na-Cl facies, and display salinities that still exceed those at Bassett's Lookout and Kibblesworth, and indeed range up to the same sorts of values as found in Eastgate No 1 (Table 1).

The similarity with Eastgate No 1 extends to the stable isotopes: the deep subsurface mine water samples analysed by Sheppard and Langley (1984) give very similar δ^{18}O and δ^2H values (Table 2) to those found at Eastgate No 1 (Table 1). In both cases, the δ^{18}O/δ^2H signatures are essentially indistinguishable from those of present-day surface waters and shallow groundwaters. For instance, surface runoff near Eastgate No 1 (in the Westernhope Burn at Brotherlee (NY 93482 37810) in July 2006) was found by the present authors to have δ^2H = −43.7‰ and δ^{18}O = −7.7‰. Similarly analysis of shallow ground waters encountered in nearby Frazer's Grove Mine gave δ^2H = −52‰ and δ^{18}O = −8.3‰ (Younger, 2000). Notwithstanding their high salinities, therefore, both the deep saline coal mine waters and the Eastgate No 1 Geothermal Borehole water have isotopic signatures that are distinctly 'meteoric'-suggesting a decoupling of the salinity from the host fluid, which is conceptually difficult to understand. This is an enigma: such isotopic values would normally be associated with fresh, recently recharged waters. So is this a fluke, or is the combination of high salinities with 'meteoric' isotope signatures more general in northern England?

5.2. The saline springs of Cumbria

Whereas mining appears to have eliminated the former surface brine springs in the northeast, further west, where mining never took place, several natural saline springs still flow at surface (Fig. 2;

Table 3

Summary of hydrochemistry of saline spring waters in Cumbria. For locations, see Fig. 2. Unless otherwise stated, concentrations are in ppm (= mg/kg). Note that the isotope results are for the water itself. n.d., not determined. Analytical data from Cooper (2011); facies designations by the present authors.

Site	Manesty	Lorton (Stanger)	Shap Spa	Gilcrux
Grid reference	NY 2517 1847	NY 1412 2719	NY 5777 0972	NY 1210 3833
Date sampled	26th July 2011	29th June 2011	29th June 2011	26th July 2011
pH	6.62	6.78	7.75	6.93
Temp. (°C)	12.3	14.2	11.6	20.1
TDS	1675	21,775	7170	2291
Ca	244	2081	1256	n.d.
Mg	9.5	197	4	n.d.
Na	369	5453	1138	n.d.
K	5.6	194	38	n.d.
SO$_4$	24.2	1.56	93	n.d.
HCO$_3$	75.6	182	102	n.d.
Cl	920	14,304	3734	n.d.
δ^2H (of water)	−43.67	−45.51	−56.20	n.d.
δ^{18}O (of water)	−6.16	−6.78	−8.56	n.d.
Facies:	Na-Ca-Cl	Na-(Ca)-Cl	Na-Ca-Cl	n.d.

Table 4

Solute concentrations in saline waters sampled at depths in excess of 1000 m in Borehole 3 (NY 026 026) at Sellafield, west Cumbria. All concentrations in ppm.

Stratigraphic unit	Sherwood Sandstone	Carboniferous Limestone	Borrowdale Volcanic Group
Depth	1106	1539	1668
TDS	188,000	135,000	177,000
Ca	2520	2610	2910
Mg	686	537	489
Na	71,600	49,300	65,100
K	327	292	539
SO$_4$	4910	4740	3340
HCO$_3$	55	184	<5
Cl	108,000	77,700	104,000
δ^2H	−32	−42	−32
δ^{18}O	−5.1	−5.8	−5.9
Facies:	Na-Cl	Na-Cl	Na-Cl

Data from Bath et al. (2006); hydrochemical facies assignations by the present authors.

Table 3). These Cumbrian saline springs have long been subject to chemical investigations (e.g. Ransome, 1848; Feather, 1966; Hamilton-Taylor et al., 1988). However, it is only recently that their stable isotope signatures have been investigated (Cooper, 2011). As shown in Table 3, the Cumbrian springs are typically of Na-Ca-Cl facies, which is exactly the same facies as at Eastgate No 1 and in the deepest of the old underground samples in the north-eastern collieries (Vane Tempest, 530 m; Table 2). They also have δ^{18}O and δ^2H signatures very similar to those of both Eastgate No 1 and the colliery waters, again indicating meteoric associations.

5.3. Depth v 'meteoricity'

Given the prior inference of dilution of deep waters by incoming fresh water, it is obvious to enquire whether depth correlates with the strength of the meteoric isotope signature. The new data presented in Table 1 span a range of depths from 170 to 1660 m, but are for three different sites. The coal mine waters presented in Table 2 also span a range of depths, as indicated, but even the mixtures of water pumped from the current pumping shafts at Bates, Dawdon and Horden are only accessing saline waters from the uppermost 600 m or so of the subsurface, as the deepest colliery shaft in the region was only 530 m deep, with workings extending a little deeper as they followed strata down-dip. The Cumbrian saline springs summarised in Table 3 are all surface outflows, for which the prior depth of groundwater circulation is unknown. Hence the data presented in Tables 1–3 are difficult to interpret in terms of depth, as they are from numerous and widespread sources. It is therefore instructive to compare these data with very high-quality data collected from a range of depths (and lithologies) within a single deep borehole. Such a comparison is afforded by the Sellafield No 3 borehole (Fig. 1, Table 4) which

was drilled in west Cumbria as part of the Nirex investigations in the 1990s (Bath et al., 1996, 2006). Table 4 presents a representative sub-set of these data. Again, high salinity is accompanied by very 'meteoric' δ^{18}O/δ^2H signatures, with no obvious trend with depth. It would thus appear that 'meteoric' water is combined with saline chemistry from shallow depths to more than 1.5 km depth.

5.4. Salinity-generating processes

The observation that high salinity coupled with 'meteoric' isotope signatures is a regional feature of groundwaters across a range of depths (≤1700 m) in northern England begs an explanation. All previous investigators are agreed that modern sea water is not a significant source of the observed salinity (Anderson, 1945; Edmunds, 1975; Sheppard and Langley, 1984). Working without the benefit of isotope data, Edmunds (1975) suggested that many of the deep mine brines represent remnants of sea water from the Carboniferous era, modified by base exchange reactions and dolomitisation, locally augmented with some degree of dissolution of (previously) overlying Permian evaporites. However, with the benefit of the 'meteoric' isotope signatures, Sheppard and Langley (1984) inferred "Pleistocene or Recent" ages for "most, if not all" of the brines. This then required them to argue that the composition of the waters are controlled by "dissolution, exchange and/or filtration processes with … minerals" and that "some of the dissolution reactions must be rapid to attain the observed high concentrations of Na and Cl". They then go on to implicate evaporite dissolution, albeit noting that "the reactions are probably quite complex" (Sheppard and Langley, 1984).

In the three decades since Sheppard and Langley (1984) reported their findings, much work has been done on the isotope
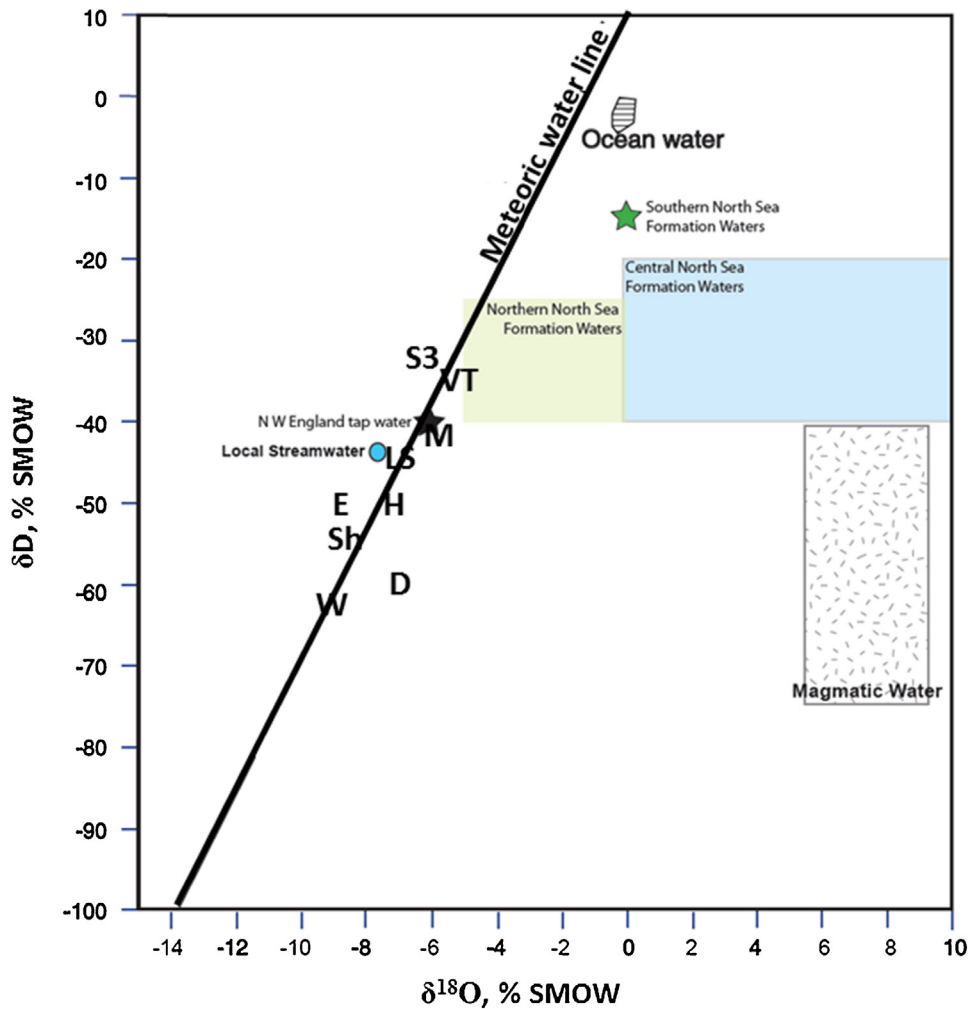
Fig. 3. Plot of δ²H versus δ¹⁸O for deep saline groundwaters and saline springs of northern England, with typical fields for waters compared with them in the discussion in the text. D, Dawdon Colliery; E, Eastgate Boreholes (1 and 2); H, Horden Colliery; LS, Lorton Stanger spring; M, Manesty spring; S3, Sellafield Borehole no 3; Sh, Shap Spa spring; VT, Vane Tempest Colliery; W, Westoe Colliery.
Data sources: D, H, VT and W, Sheppard and Langley (1984); LS, M, Sh, Cooper (2011); S3, Bath et al. (2006); E, this study.

systematics of many different geological settings in northern England, including those associated with evaporite dissolution (e.g. Bottrell et al., 1996, 2006) and complex basinal histories in the North Sea oilfields (e.g. Ziegler et al., 2001). It is therefore possible to place the isotopic signatures of the onshore (and near-shore subsea coal mine) brines presented in Tables 1–4 in a wider context, as shown in Fig. 3. This plot makes it clear that the onshore brines of northern England are:

- Certainly not associated with modern sea water.
- Not affiliated with the central North Sea subsurface brines (which reflect a complex history of uplift, erosion and subsidence).
- Not typical of waters that have been involved in dissolution of Permian evaporites.

The lack of evaporite participation in the origin of the Eastgate No 1 waters is corroborated by the sulphate isotope data (3.3‰ for sulphate sulphur, and −3.9‰ for sulphate oxygen). These differ markedly from those reported by Bottrell et al. (2006) for Coal Measures brines and evaporite sources in Northern England. Such low sulphate sulphur δ³⁴S values are very different from those typical of sulphate mineral deposits in the UK (typically around +20‰, clearly reflecting ultimately marine origins) but are similar to those reported for magmatic (granitic) sulphur *sensu stricto* (Lowry et al., 2005).

So much for what the sulphur isotope tell us is *not* the case: what positive inferences can be drawn from them? The most obvious postulate would be granite-derived sulphur; yet the work of Lowry et al. (2005) has revealed that the Weardale Granite is considerably richer in ³⁴S than the Eastgate No 1 waters, with no result lower than 5‰ – and most being well above that value. This is consistent with the fact that the Weardale Granite is peraluminous ("S-type"), i.e. reflecting considerable assimilation of crustal components prior to crystallisation, overprinting the typical magmatic signature. However, sulfide S isotope data for the nearby Shap Granite are consistent with the Eastgate no 1 values, having a restricted range from −0.3 to +4.5. The inference is thus that the sulfate in these deep saline waters could be derived from oxidation of ultimately granite-sourced sulfide. It is not credible that this oxidation is ongoing at depth, given the lack of dissolved oxygen; but the inference is consistent with ancient ingress of oxygen-bearing meteoric water, capable of oxidising modest amounts of sulphide.

Clearly some enhanced and/or prolonged rock–water reactions within the local succession need to be invoked to explain the high salinities (cf Leybourne and Goodfellow, 2007; Kietäväinen et al., 2011; Bucher et al., 2012). Further clues as to the nature of these reactions are afforded by the elevated Ca concentrations in the brines of Eastgate No 1 (Table 1), the deepest of the colliery brines (e.g. Vane Tempest, Table 2; see also Edmunds), and the Cumbrian saline springs (Table 3). Calcium enrichment in the brines of

northern England was commented on by Ransome (1848), discussing a saline water encountered in a mine that was at that time working in the neighbourhood of the Manesty spring: "... the peculiarity of the water is the large quantity of chloride of calcium which it contains ..." A century later, discussing the elevated Ca concentrations in coal mine brines, Anderson (1945) commented "...It remains to find the source of the calcium chloride. This salt does not enter into the proximate formula of the salts in the modern ocean; nevertheless, even if all the calcium were present as the chloride, it would amount to less than one-sixth of the average found in the chloride waters ... It is noteworthy that in 1842 the Wallsend Spring on Tyneside, with a salinity thrice that of the ocean, ran 100 per cent calcium chloride with traces of the chlorides of sodium and magnesium, whereas six years later, only 30 per cent of the salt was present, the remainder being sodium chloride with a trace of magnesium chloride. Analyses of many other British chloride waters show that a change took place in the sodium-calcium ratio from time to time. Thus it seems that a deep-seated origin for the calcium chloride must be sought. It need not necessarily be a primary solution, but may be the result of the passage of liquors, containing reactive chlorine ions, through formations of limestone ..."

What can we make of all of this today, in the light of the isotopic evidence that indicate a meteoric origin for the highly saline Na-Ca-Cl brines? Firstly, to understand the timescales over which meteoric water intrusion into the subsurface would have been possible in this region, we need to acknowledge the extent and rate of regional Cenozoic uplift and denudation - which has recently been more tightly constrained using fission-track evidence from the Eastgate No 1 Borehole itself (Green et al., 2012). The disposition of the Weardale Granite (Kimball et al., 2010) viz-a-viz the Carboniferous sediments (Manning et al., 2007) is such that Cenozoic uplift will have imposed subsurface hydraulic gradients both into and out of overlying limestones at different times, with head gradients being held in particular polarities for millennia at a time. Thus, though the Tertiary meteoric water will sometimes have been introduced to the granite from the limestones, and at other times it may have been expelled into it. Such slow 'flushing' cycles could explain the elevated calcium concentrations in the brines now found in the granite. While it is conceivable that the mudstone intervals in the Carboniferous could have offered some degree of 'membrane filtration', Edmunds (1975) has previously presented evidence that suggests this was very limited or non-existent. More likely, the presence of discrete permeable faults will have allowed fairly rapid vertical transfer (advective, convective or in response to density contrasts), followed by slow lateral diffusion. The elevated geothermal gradient in the radio-thermal Weardale granite can be expected to have favoured thermal convection (e.g. Dunham, 1990; Cann and Banks, 2001; Manning et al., 2007). Prolonged and intensified rock–water reactions, with dissolution rates favoured by elevated tempera-tures, could explain most of the observed chemistry, without the need to invoke a marine or evaporite-dissolution precursor water (cf Leybourne and Goodfellow, 2007; Kietäväinen et al., 2011; Bucher et al., 2012). Thus it at least conceivable that the present chemical composition of the northern England saline ground-waters is at least partly explicable by sustained reaction of meteoric waters with rocks throughout the Tertiary, under the influence of locally high temperatures sustained by radiothermal heat production in the Wearale and Shap Granites, for instance.

5.5. Quaternary freeze-out?

During the cold periods of the Quaternary, the salinity may have been further intensified by a cold-climate process: the phenome-non of in situ "freeze-out" beneath permafrost bodies (Starinsky and Katz, 2003; Stotler et al., 2009, 2012), in which "*solutes concentrate in residual fluids and isotopes fractionate between ice and residual fluids during freezing ...*" (Stotler et al., 2012). Variously advocated (Starinsky and Katz, 2003; Casanova et al., 2005) and disputed (Stotler et al., 2012) as an explicatory process for the widespread occurrence of saline groundwaters in the Precambrian shield regions of North America and northern/central Europe, the extent of freeze-out beneath Quaternary and modern permafrost remains controversial. Yet the process has recently been confirmed to be operating beneath pack ice in surface waters of the Canadian Arctic, notably in shallow coastal lakes that lack free connectivity to the open ocean (Grasby et al., 2013). Similarly, in Antarctica, Frank et al. (2010) discovered that the same process, operating in lagoons with limited connectivity to the open sea in McMurdo Sound, had resulted in the formation of brines which had penetrated by density-driven flow more than 200 m down through permeable sediments. Nearby, in the McMurdo Dry Valleys, Toner and Sletten (2013) report widespread occurrence of Ca-Cl brines in the shallow subsurface, attributing their distinctive chemistry to formation of Na-Cl brines beneath ground ice which then exchanges Na for Ca during infiltration. A similar mechanism operating during Quaternary cold periods might in part explain the notable Ca content of many northern English deep brines. Certainly, the very high Ca/HCO_3^- ratios in the Eastgate No 1 waters (Table 1), the deep colliery waters (Table 2) and the Cumbrian saline springs (Table 3) is consistent with a Ca-enrichment process other than limestone dissolution.

How thick may permafrost have been in this region during the Quaternary cold stages? A range of factors influence permafrost thickness, including the extent and duration of sub-zero ambient temperatures; topography; terrestrial heat flow; permeability distributions; antecedent groundwater flow patterns; and the presence or absence of overlying glaciers, and (if present) whether these were wet- or dry-based (Williams and Smith, 1989). To take just one site for which we have coincidental data on heat flow and brine chemistry (i.e. Eastgate No 1; Fig. 2), then using a simplified approach (Williams and Smith, 1989; Younger, 1993b) permafrost thickness may be estimated as follows:

$$Z_p = \frac{(O\,^\circ C - T_s)K_T}{Q_g}$$

where Z_p is the thickness of the permafrost (m); $O\,^\circ C$ represents the freezing point of water at zero degrees Celsius; T_s is mean ground surface temperature (°C) at the relevant point in history; K_T is thermal conductivity of the rock (W m^{-1} °C^{-1}), and Q_g is geothermal heat flux (W m^{-2}), which equals the product of the geothermal gradient (°C km^{-1}) and K_T.

If it assumed that present-day value for Q_g as modelled from downhole measurements at Eastgate (i.e. 0.1164 W m^{-2}; West-away and Younger, 2013) is valid for the Quaternary as a whole (which seems reasonable in view of the local history of cooling detected from fission-track data obtained from this very borehole; Green et al., 2012), and assuming a mean thermal conductivity value for the sequence penetrated Weardale Granite of around $K_T = 2.99$ W m^{-1} °C^{-1} (following Westaway and Younger, 2013), then it only remains to estimate the mean annual ground surface temperature in this region during the cold periods of the Quaternary. This is problematic, as it is likely to have been between 8 and 18 °C lower than the present mean annual air temperature depending on whether or not a glacier was present at surface. Given its elevation in the Pennine Hills at about 250 m above Ordnance Datum, the present-day mean annual air temperature at Eastgate is somewhat cooler than the UK average, at about 8 °C. Using both extremes of past temperature deviation, T_s may have ranged from near zero when wet-based glaciers were

present to and −10 °C otherwise. This in turn means that permafrost may have ranged from zero to about 250 m thickness in the Eastgate area. Given that the granite lies 273 m below ground at Eastgate No 1, this means that, during periods of maximum permafrost development, freeze-out processes could have expelled saline waters from almost the entire sedimentary cover into the Weardale Granite. Noting that lowermost part of the sedimentary sequence is particularly rich in limestone (Manning et al., 2007), the relative enrichment of the Eastgate brines in calcium is consistent with this process.

5.6. Implications for geothermal exploration and development

The geothermal potential of the UK has been estimated at a total of about 150 Gigawatts (GW), comprising 140 GW$_{th}$ for direct heat use applications and about 10 GW$_e$ suitable for electricity generation (SKM, 2012). To put these figures in perspective, they amount to around twice the present total UK heat demand, and about 25% of current UK electricity demand. Unlike most renewables, geothermal energy is available constantly, irrespective of time of day (which affects solar), weather (affects solar and wind) or season (which affects solar, wind and hydropower). On this basis, geothermal energy ought to be able make a significant contribution to a future low-carbon energy economy in the UK, though development to date has been spasmodic and slow (Younger et al., 2012; Rybach, 2014), mainly due to the high upfront costs for drilling, exacerbated by the uncertainty of success in the early stages of exploration and development of a new reservoir. While the same is also true of hydrocarbon reservoirs, the value and global marketability of the sought commodity more easily bears these costs in that case, in contrast to geothermal, which essentially produces steam and/or hot water, which can only be used near to the boreholes. As with any reservoir, attainment of sustained production depends on the development of a robust conceptual model, consistent with all available data, which allows reasonable predictions to be made of long-term evolution of fluid pressures (= heads) and – especially in the case of geothermal – temperatures. A properly developed geothermal reservoir will operate on the basis of an "open loop", in which hot water/steam is produced from certain boreholes, and spent, cooler water is later reinjected into others (e.g. Garnish and Brown, 2012). Reinjection serves two principal purposes:

(i) It helps maintain reservoir pressures in the long-term, avoiding a gradual increase in pumping heads/steam production pressures which can render an initially promising geothermal reservoir uneconomic (Dickson and Fanelli, 2005).
(ii) It avoids the environmental disbenefits of disposing of warm, saline waters in the surface environment, where they may be detrimental to freshwater ecosystems and potable water supplies (DiPippo, 2012).

Getting the coupled abstraction–reinjection process right is far from trivial: reinject too close to source and thermal breakthrough of cooler waters to the production wells may occur, detracting from the utility of the produced waters; reinject too far away and you may fail to maintain adequate reservoir temperatures in the production zone. Hydrochemical data can provide crucial insights into patterns of geothermal fluid movement within reservoirs (e.g. Ármannsson, 2010). Hence this preliminary study offers something of a baseline for northern England, against which future studies of reservoir fluid evolution might be compared. Hydrochemical data are also crucial in planning to prevent/minimise corrosion and/or scale accumulation in pumps, heat-exchangers and pipework – one of the biggest potential pitfalls in development of deep geothermal energy (e.g. DiPippo, 2012).

On the basis of the data presented in Tables 1 and 3, it is clear that development of deep geothermal resources in northern England will necessitate implementation of corrosion prevention measures during pumping, heat-exchange and reinjection operations. These measures are likely to include equipping all metallic infrastructure that contacts the geothermal fluids with galvanic protection, as well taking steps to prevent oxygen ingress into boreholes, tanks and pipelines.

Hydrochemistry of deep groundwaters also holds forth the possibility of estimating the temperatures at which observed solute ratios were acquired, which can be a useful indicator of current subsurface temperature distributions (e.g. Ármannsson, 2010; Powell and Cumming, 2010; Younger, 2014). Ideal application of hydrochemical "geothermometers" (e.g. Powell and Cumming, 2010) requires detailed site-specific analysis, preferably including a robust understanding of likely order-of-encounter between groundwater and rocks of a known mineralogical composition along the flowpath leading to the borehole or spring sampled. Such a level of understanding is generally lacking in the early stages of geothermal exploration, which is certainly how the current state of play in northern England would have to be characterised. The geochemical equilibrium models, upon which geothermometric calculations are based, assume that the groundwater sampled at a given point has encountered idealised (i.e. stoichiometric end-member) minerals *en route* to its sampling point. For instance, most Na-K based geothermometers assume that equilibration with plagioclase and potassium feldspars has been feasible; since these minerals are known to be present (and in the case of K-feldspars, abundant) in the Eastgate and Shap granites in northern England, one would suppose that such models would be applicable there. To a first approximation, then, it may be instructive to compare the predicted temperatures at which the various waters last achieved geochemical equilibrium during their transport to their sampling points. Note that this is *not* the same thing as the maximum temperature they may ever have attained: re-equilibration at a lower temperature may well have occurred since then. Hence the geothermometric temperature estimates are best understood as the minimum estimate for the peak temperatures the various waters have previously experienced. The available data are insufficient to support many of the widely used geothermometric models (e.g. those involving silica). Furthermore, existing geothermometric calculations are based on the well-known Debye-Hückel ionic association model, which is only valid for salinities up to about that of sea water (Appelo and Postma, 2005). Hence the hyper-saline waters in Table 2 are not amenable to this analysis. Ideally, full speciation modelling of the waters should be undertaken prior to calculating apparent equilibration temperatures. However, for Na-K models, the activities of those two ions tend to be closely approximated by their total molalities, so that it is possible to apply the Fournier (1979) model using molalities calculated from reported dissolved concentrations in ppm. This having been done, the model of Fournier (1979) has been applied to all the waters listed in Table 5.

These results suggest that temperatures in the range of 80 to 190 °C are widely attained within a few kilometres of surface across much of northern England. The samples displaying the lower temperatures (Manesty and Bassett's Lookout) are the very sites in which dilution of the saline water by shallow-sourced modern-day recharge through old mine workings is expected, given present field relations. Eliminating those two sites from the list would narrow the range of inferred subsurface temperatures to 122–190 °C. This is significant, as 120 °C is widely regarded as the temperature at which the use of binary-cycle power plants (operating according to the Organic Rankine Cycle, or the similar Kalina Cycle; DiPippo, 2012) becomes comfortably economically viable. This means that if the zones in which waters are currently

Table 5
Liquid-based geothermometry of saline waters in northern England (see Tables 1–3) using the Na-K geothermometer of Fournier (1979), which in practical terms reduces to the following form: $T\,^{\circ}C = (1217/(1.483 + \log([Na]/[K]))) - 273.15$.

Site	Na (ppm)	Na (molal)	K (ppm)	K (molal)	Estimated temperature when last at equilibrium (°C)
Eastgate No 1	9630	4.19E−01	720	2.39E−02	173.2
Science Central	1166	5.07E−02	110	3.65E−03	190.4
Bassetts Lookout	4690	2.04E−01	91	3.02E−03	94.3
Manesty	369	1.61E−02	5.6	1.86E−04	82.8
Lorton (Stanger)	5453	2.37E−01	194	6.45E−03	126.0
Shap Spa	1138	4.95E−02	38	1.26E−03	122.4
Horden pumped	9200	4.00E−01	514	1.71E−02	153.4
Dawdon pumped	13,800	6.00E−01	935	3.11E−02	166.3
Bates pumped	2010	8.74E−02	94	3.12E−03	142.2

experiencing such temperatures can be accessed by drilling, then efficient combined heat and power plants could be widely developed in the region using these deep geothermal resources. To judge from geothermal gradients recorded at Eastgate and Science Central (~36 °C per kilometre; Manning et al., 2007; Younger, 2013), then given annual average ambient temperatures at surface of around 10 °C, one might expect to encounter suitable temperatures at depths of 3–5 km. At shallower depths (~2 km), waters with temperatures in excess of 80 °C are likely to be encountered.

As exploitation of the deep geothermal reservoirs proceeds, it will be crucial to implement regular sampling of the produced fluids with comprehensive analysis covering major cations and anions plus stable isotopes. In addition to those reported here, it would also be beneficial to consider the stable isotopes of boron (fractionation of which is apparently diagnostic of former permafrost freeze-out; Casanova et al., 2005), radiocarbon and other indicators of groundwater age (Elliot, 1990). Though difficult to apply and interpret, the latter could finally shed some light on the long-standing debate over how long ago these waters were recharged (Edmunds, 1975; Sheppard and Langley, 1984), as well as allowing adjudication of the possible contribution of Quaternary permafrost freeze-out on these waters, and facilitating the addition of a palaeoclimatic perspective to their thorough interpretation. In addition, detailed halogen analyses (Cl, Br ± I) would assist in identifying the pathways of salinity development, independent of the nature of the decoupled meteoric water signatures found in these natural ground waters (e.g. Fontes and Mattray, 1993; Banks et al., 2002). Such insights would help constrain reservoir conceptual models, and quantify (or dismiss) any element of modern recharge (cf Elliot, 1990).

6. Conclusions

Although the seminal paper of Anderson (1945) represented the advent of a modern geochemical approach to the study of chloride-rich saline groundwaters in northern England, their existence had long been noted (e.g. Ransome, 1848), and some of their drawbacks to industry described (Dunn, 1877; Clowes, 1889). In the last few decades it has become increasingly apparent that these saline waters are widespread in the region, often occurring at depths of just a few hundred metres (e.g. in Eastgate No 1 and Bassett's Lookout boreholes), and still giving rise to surface springs in rural Cumbria where (unlike in the case of former saline springs in urban Tyneside) they have been largely unaffected by the hydrogeological disruption caused by large-scale mining (Manesty being the exception to this). Initially the focus of research was on understanding whether these saline groundwaters represent remnants of possible mineralising fluids for orebodies found in the North Pennines (e.g. Dunham, 1990). A more applied use was detecting the provenance of waters entering subsea coal mine workings (Edmunds, 1975), in particular checking whether they

were sea waters (they never were). The geochemistry of offshore brines then became an important issue in deducing hydrocarbon reservoir "plumbing", as well as in assessing corrosion and scale accretion risks. The most recent motivation is in geothermal exploration, in which the North East is the only part of the UK to see any renewed deep drilling in the last thirty years. As with hydrocarbon investigations, the chemistry of the saline waters encountered is of more than pure curiosity value, as different possible origins imply different total volumes of water in storage, with implications for geothermal resource quantification, and corrosion and scaling management. Though hydrogeochemical data are as yet sparse, it is already clear that these geothermal fluids and saline springs differ markedly from offshore oilfield brines in their isotopic signatures. They are distinctly meteoric in their $\delta^{18}O$ and $\delta^{2}H$ signatures which strikes a conceptual discord with their-often intense-salinity. Both O and H isotopes and $\delta^{34}S$ allow us to rule out evaporite dissolution as a significant source of their salinity. This is at odds with many North Sea oilfield brines, where such contributions are widespread. The enigma of 'meteoric' waters with very high salinities is not yet fully understood, but evidence adduced in this paper suggests a combination of processes, including cryogenic concentrations of brines beneath Quaternary permafrost, and vigorous rock–water reactions, influence by locally high subsurface temperatures, extending back through the period of Cenozoic uplift and denudation. We are only at now beginning to really get to grips with these paradoxical saline waters, yet a broad understanding of their origins and behaviour will be essential to the success of the emerging UK geothermal industry.

References

Anderson, W., 1945. On the chloride waters of Great Britain. Geological Magazine 82, 267–274.

Andrews, J.N., Kay, R.L.F., 1983. The U contents and $^{234}U/^{238}U$ activity ratios of dissolved uranium in groundwaters from some Triassic Sandstones in England. Isotope Geoscience 1, 101–117.

Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, 2nd ed. CRC/A.A. Balkema Publishers, Leiden, NL 536 pp.

Ármannsson, H., 2010. Application of Geochemical Methods in Geothermal Exploration. Notes for Short Course V (Exploration for Geothermal Resources), organised by the United Nations University Geothermal Training Programme, the Geothermal Development Company (Kenya) and KenGen. Lake Bogoria and Lake Naivasha, Kenya, October 29–November 19. 8 pp. Available at: www.os.is/gogn/unu-gtp-sc/UNU-GTP-SC-11-27.pdf (accessed 09.08.13).

Armstrong, W., 1856. On the constitution and action of the chalybeate mine waters of Northumberland and Durham. Transactions of the North of England Institute of Mining Engineers 4, 271–281.

Back, W., 1960. Origin of hydrochemical facies of ground water in the Atlantic Coastal Plain. In: Proceedings of the 21st International Geological Congress, Copenhagen, Denmark. Part 1, pp. 87–95.

Back, W., 1961. Techniques for mapping of hydrochemical faciesIn: United States Geological Survey Professional Paper 14214-D, pp. 380–382.

Banks, D.A., Boyce, A.J., Samson, I.M., 2002. Constraints on the origins of fluids forming Irish-Zn-Pb-Ba deposits: Evidence from the chemistry of fluid inclusions. Economic Geology 97, 471–480.

Banks, D., Younger, P.L., Dumpleton, S., 1996. The historical use of mine-drainage and pyrite-oxidation waters in central and eastern England, United Kingdom. Hydrogeology Journal 4, 55–68.

Bath, A.H., McCartney, R.A., Richards, H.G., Metcalfe, R., Crawford, M.B., 1996. Groundwater chemistry in the Sellafield area: a preliminary interpretation. Quarterly Journal of Engineering Geology 29, S39–S57.

Bath, A., Richards, H., Metcalfe, R., McCartney, R., Degnan, P., Littleboy, A., 2006. Geochemical indicators of deep groundwater movements at Sellafield, UK. Journal of Geochemical Exploration 90, 24–44.

Bottrell, S.H., Leosson, M.A., Newton, R.J., 1996. Origin of brine inflows at Boulby potash mine, Cleveland, England. Transactions of the Institution of Mining and Metallurgy 105, B151–B164.

Bottrell, S.H., West, L.J., Yoshida, K., 2006. Combined isotopic and modelling approach to determining the source of saline groundwaters in the Selby Triassic sandstone aquifer, UK. Geological Society, London, Special Publications 263, 325–338, http://dx.doi.org/10.1144/GSL.SP.2006.263.01.19.

Bjørlykke, K., Gran, K., 1994. Salinity variations in North Sea formation waters: implications for large-scale fluid movements. Marine and Petroleum Geology 11, 5–9.

Bucher, K., Stober, I., Seelig, U., 2012. Water deep inside the mountains: unique water samples from the Gotthard rail base tunnel, Switzerland. Chemical Geology 334, 240–253.

Cann, J.R., Banks, D.A., 2001. Constraints on the genesis of the mineralization of the Alston Block, Northern Pennine Orefield, northern England. Proceedings of the Yorkshire Geological Society 53, 187–196.

Casanova, J., Négrel, P., Blomqvist, R., 2005. Boron isotope fractionation in groundwaters as an indicator of past permafrost conditions in the fractured crystalline bedrock of the Fennoscandian shield. Water Research 39, 362–370.

Chandler, R.L., McWhorter, D.B., 1975. Upconing of the fresh-water–salt-water interface beneath a pumping well. Ground Water 13, 354–359.

Clowes, F., 1889. Deposits of barium sulfate from mine water. Proceedings of the Royal Society 46, 368–369.

Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. Analytical Chemistry 28, 199–260.

Cooper, N., 2011. Saline Springs in Cumbria. (Unpublished M.Sc. thesis)Hydrogeology, University of Birmingham 83 pp.

Craddock-Hartopp, M.A., Holliday, D.W., 1984. The Fell Sandstone Group of Northumberland: Invesigation of the geothermal potential of the UK. British Geological Survey Keyworth 34 pp.

Darling, W.G., Edmunds, W.M., Smedley, P.L., 1997. Isotopic evidence for palaeowaters in the British Isles. Applied Geochemistry 12, 813–829.

Dickson, M.H., Fanelli, M., 2005. Geothermal Energy: Utilization and Technology. Earthscan, London 224 pp.

DiPippo, R., 2012. Geothermal Power Plants: Principles, Applications, Case Studies and Environmental Impact, 3rd ed. Butterworth-Heinemann, Oxford 624 pp.

Donnelly, T., Waldron, S., Tait, A., Dougans, J., Bearhop, S., 2001. Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer. Rapid Communications in Mass Spectrometry 15, 297–1303.

Downing, R.A., Gray, D.A., 1986. The geothermal resources of the United Kingdom. Journal of the Geological Society 143 (3), 499–507.

Dunham, K.C., 1990. Geology of the Northern Pennine Orefield; Volume 1 Tyne to Stainmore. In: Economic Memoir of the British Geological Survey, England and Wales, Sheets 19 and 25, and Parts of 13, 24, 26, 31, 322nd ed., 299 pp.

Dunn, J.T., 1877. On a water-box deposit. Chemical News 35, 140.

Edmunds, W.M., 1975. Geochemistry of brines in the Coal Measures of north east England. Transactions of the Institution of Mining and Metallurgy (Section B: Applied Earth Sciences) 84, 39–52.

Edmunds, W.M., Andrews, J.N., Burgess, W.A., Kay, R.L.F., Lee, D.J., 1984. The evolution of saline and thermal groundwaters in the Carnmenellis granite. Mineralogical Magazine 48:, 407–424.

Edmunds, W.M., Robins, N.S., Shand, P., 1998. The saline waters of Llandrindod and Builth, Central Wales. Journal of the Geological Society London 155, 627–637.

Elliot, T., 1990. Geochemical Indicators of Groundwater Ageing. (Unpublished Ph.D. thesis)School of Chemistry, University of Bath, UK 429 pp.

Elliot, T., Younger, P.L., 2007. Hydrochemical and isotopic tracing of mixing dynamics and water quality evolution under pumping conditions in the mine shaft of the abandoned Frances Colliery, Scotland. Applied Geochemistry 22, 2834–2860.

Feather, S.W., 1966. Saline spring, Brandlehow Mine, near Keswick. In: Memoirs of the Northern Cavern and Mine Research SocietyMemoirs, , pp. 53–54.

Fontes, J.C., Matray, J.M., 1993. Geochemistry and origin of formation brines from the Paris basin, France, 1 Brines associated with Triassic salts. Chemical Geology 109, 149–175.

Fournier, R.O., 1979. A revised equation for the Na/K geothermometer. Geothermal Resources Council Transactions 3, 221–224.

Frank, T.D., Gui, Z., the ANDRILL SMS Science Team, 2010. Cryogenic origin for brine in the subsurface of southern McMurdo Sound, Antarctica. Geology 38, 587–590, http://dx.doi.org/10.1130/G30849.1.

Galloway, R.L., 1904. Annals of Coal Mining and the Coal Trade. Volume 2 (Second Series, 1836–1850) Colliery Guardian Company Ltd., London 409 pp. (Reprinted 1971 by David & Charles, Newton Abbot).

Garnish, J., Brown, G., 2012. Chapter 9. Geothermal energy. In: Boyle, G. (Ed.), Renewable Energy. Power for a Sustainable Future. 3rd ed. Open University/ Oxford University Press, Oxford, pp. 409–459.

Grasby, S.E., Smith, I.R., Bell, T., Forbes, D.L., 2013. Cryogenic formation of brine and sedimentary mirabilite in submergent coastal lake basins, Canadian Arctic. Geochimica et Cosmochimica Acta 110, 13–28.

Green, P.F., Westaway, R., Manning, D.A.C., Younger, P.L., 2012. Cenozoic cooling and denudation in the North Pennines (northern England, UK) constrained by apatite fission-track analysis of cuttings from the Eastgate Borehole. Proceedings of the Geologists' Association 123, 450–463.

Hall, A.J., Boyce, A.J., Fallick, A.E., Hamilton, P.J., 1991. Isotopic evidence of the depositional environment of Late Proterozoic stratiform barite mineralisation, Aberfeldy. Scotland. Chemical Geology (Isotope Geoscience) 87, 99–114.

Hamilton-Taylor, J., Edmunds, W.M., Darling, W.G., Sutcliffe, D.W., 1988. A diffusive ion flux of non-marine origin in Cumbrian lake sediments: implications for element budgets in catchments. Geochimica et Cosmochimica Acta 52, 23–227, http://dx.doi.org/10.1016/0016-7037(88)90071-3.

Headworth, H.G., Puri, S., Rampling, B.H., 1980. Contamination of a Chalk aquifer by mine drainage at Tilmanstone, East Kent, UK. Quarterly Journal of Engineering Geology and Hydrogeology 13, 105–117, http://dx.doi.org/10.1144/GSL.QJEG.1980.013.02.05.

Howard, K.W.F., Lloyd, J.W., 1983. Major ion characterization of coastal saline ground waters. Ground Water 21, 429–437.

Kietäväinen, R., Lasse, A., Kukkonen, I.T., Hendriksson, N., Nyyssönen, M., Itävaara, M., 2011. Characterisation and isotopic evolution of saline waters of the Outokumpu Deep Drill Hole. Finland – implications for water origin and deep terrestrial biosphere. Applied Geochemistry 32 (Special issue S1), 37–51.

Kimball, G.S., Young, B., Millward, D., Crowley, Q.G., 2010. The North Pennine batholith (Weardale Granite) of northern England: new data on its age and form. Proceedings of the Yorkshire Geological Society 58, 107–128.

Lemon, R., 1991, March. Pumping and disposal of deep strata mine water. Mining Technology 69–76.

Leybourne, M.I., Goodfellow, W.D., 2007. Br/Cl ratios and O, H, C, and B isotopic constraints on the origin of saline waters from eastern Canada. Geochimica et Cosmochimica Acta 71, 2209–2223.

Lloyd, J.W., Rushton, K.R., Taylor, H.R., Barker, R.D., Howard, K.W.F., 1978. Saline groundwater studies in the Chalk of Northern Lincolnshire. In: Wilkinson, W.B., Oakes, D.B., Downing, R.A. (Eds.), Proceedings of the 5th Salt Water Intrusion Meeting (SWIM). Water Research Centre, Medmenham, UK, 4–6th April 1977, pp. 89–97.

Lowry, D., Boyce, A.J., Fallick, A.E., Stephens, W.E., Grassineau, N.V., 2005. Terrane and basement discrimination in northern Britain using sulphur isotopes and mineralogy of ore deposits. In: McDonald, I., Boyce, A.J., Butler, I.B., Herrington, R.J., Polya, D.A (Eds.), Mineral Deposits and Earth Evolution. Geological Society, London, Special Publications, vol. 248. pp. 133–151.

Manning, D.A.C., Strutt, D.W., 1990. Metallogenetic significance of a North Pennine springwater. Mineralogical Magazine 54, 629–636.

Manning, D.A.C., Younger, P.L., Smith, F.W., Jones, J.M., Dufton, D.J., Diskin, S., 2007. A deep geothermal exploration well at Eastgate, Weardale, UK: a novel exploration concept for low-enthalpy resources. Journal of the Geological Society 164, 371–382.

McCartney, R.A., Winefield, O., Webb, P., Kuhn, O., 2004. Spatial variations in the composition of formation waters from the central North Sea: implications for fluid flow in the deep high-pressure high-temperature hydrocarbon play. In: Cubitt, J.M., England, W.A., Larter, S. (Eds.), Understanding Petroleum Reservoirs: Towards an Integrated Reservoir Engineering and Geochemical Approach. Geological Society, London, Special Publications, vol. 237. pp. 283–303.

McCay, A.T., Harley, T.L., Younger, P.L., Sanderson, D.C.W., Cresswell, A.J., 2014. Gamma-ray spectrometry in geothermal exploration: state of the art techniques. Energies 7 (8), 4757–4780, http://dx.doi.org/10.3390/en7084757.

Munz, I.A., Johansen, H., Huseby, O., Rein, E., Scheire, O., 2010. Water flooding of the Oseberg Øst oil field. Norwegian North Sea: application of formation water

chemistry and isotopic composition for production monitoring. Marine and Petroleum Geology 27, 838–852.

Nelson, S.T., 2000. A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. Rapid Communications in Mass Spectrometry 14, 1044–1046.

Powell, T., Cumming, W., 2010. Spreadsheets for Geothermal Water and Gas Geochemistry. Thirty-Fifth Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 1-3, 2010. SGP-TR-188. https://pangea.stanford.edu/ERE/pdf/IGAstandard/SGW/2010/powell.pdf.

Ransome, T., 1848. Analysis of a saline spring in a lead mine near Keswick. Manchester Literary and Philosophical Society Journal Series 2 8, 39.

Richter, B.C., Kreitler, C.W., 1991. Identification of sources of ground-water salinization using geochemical techniques. In: US EPA Report EPA/600/2-91/064United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada Oklahoma, 259 pp.

Robins, N.S., Smedley, P.L., 2013. Groundwater: medicine by the glassful? In: Duffin, C.J., Moody, R.T.J., Gardner-Thorpe, C., (Eds.), A History of Geology and Medicine. Geological Society, London, Special Publications, vol. 375. pp. 261–267.

Rybach, L., 2014. Geothermal power growth 1995–2013—a comparison with other renewables. Energies 7 (8), 4802–4812, http://dx.doi.org/10.3390/en7084802.

Sheppard, S.M.E., Langley, K.M., 1984. Origin of saline formation waters in northeast England: application of stable isotopes. Transactions of the Institution of Mining and Metallurgy 93, B195–B201.

SKM, 2012. Geothermal energy potential in Great Britain and Northern IrelandIn: A Report by Sinclair Knight Merz in Association with the Renewable Energy Association, London, 149 pp.

Starinsky, A., Katz, A., 2003. The formation of natural cryogenic brines. Geochimica et Cosmochimica Acta 67, 1475–1484.

Stotler, R.L., Frape, S.K., Ruskeeniemi, T., Ahonen, L., Paananen, M., Onstott, T.C., Hobbs, M.Y., 2009. Hydrogeochemistry of groundwaters at and below the base of thick permafrost at Lupin, Nunavut, Canada. Journal of Hydrology 373, 80–95.

Stotler, R.L., Frape, S.K., Ruskeeniemi, T., Pitkänen, P., Blowes, D.W., 2012. The interglacial–glacial cycle and geochemical evolution of Canadian and Fennoscandian Shield groundwaters. Geochimica et Cosmochimica Acta 76, 45–67.

Tellam, J.H., 1995. Hydrochemistry of the saline groundwaters of the lower Mersey Basin Permo-Triassic sandstone aquifer, UK. Journal of Hydrology 165, 45–84.

Tellam, J.H., Lloyd, J.W., 1986. Problems in the recognition of seawater intrusion by chemical means: an example of apparent chemical equivalence. Quarterly Journal of Engineering Geology 19, 389–398.

Toner, J.D., Sletten, R.S., 2013. The formation of Ca-Cl-rich groundwaters in the Dry Valleys of Antarctica: field measurements and modeling of reactive transport. Geochimica et Cosmochimica Acta 110, 84–105.

Turner, B.R., Younger, P.L., Fordham, C.E., 1993. Fell Sandstone Group lithostratigraphy southwest of Berwick-upon-Tweed: implications for the regional development of the Fell Sandstone. Proceedings of the Yorkshire Geological Society 49, 269–281.

Warren, E.A., Smalley, P.C., 1993. The chemical composition of North Sea formation waters: a review of their heterogeneity and potential applications. In: Parker, J.R. (Ed.), Petroleum Geology of Northwest Europe: Proceedings of the 4th Conference. Geological Society, London, pp. 1347–1352.

Warren, E.A., Smalley, P.C., 1994. North sea formation water atlas. Geological Society, London, Memoir 15, 208.

Watson, S.J., Burgess, W.G., Barker, J.A., 2012. Re-evaluating dual-porosity effects at the site of a seminal groundwater modelling study: Tilmanstone, southern England. Geological Society, London, Special Publications 364, 227–248, http://dx.doi.org/10.1144/SP364.15.

Westaway, R., Younger, P.L., 2013. Accounting for palaeoclimate and topography: a rigorous approach to correction of the British geothermal dataset. Geothermics 48, 31–51.

Worden, R.H., Manning, D.A.C., Bottrell, S.H., 2006. Multiple generations of high salinity formation water in the Triassic Sherwood Sandstone: Wytch Farm oilfield, onshore UK. Applied Geochemistry 21, 455–475.

Williams, P.J., Smith, M.W., 1989. The Frozen Earth. Fundamentals of Geocryology. Cambridge University Press, Cambridge 306 pp.

Younger, P.L., 1993a. Possible environmental impact of the closure of two collieries in County Durham. Journal of the Institution of Water and Environmental Management 7, 521–531.

Younger, P.L., 1993b. Palaeohydrogeological reconstructions of the North Lincolnshire Chalk, UK, for the last 140,000 years – comment. Journal of Hydrology 143, 505–510.

Younger, P.L., 1995a. Hydrogeology. Chapter 11. In: Johnson, G.A.L. (Ed.), Robson's Geology of North East England. (The Geology of North East England, Second Edition), Transactions of the Natural History Society of Northumbria, 56 (5), pp. 353–359.

Younger, P.L., 1995b. Hydrogeochemistry of minewaters flowing from abandoned coal workings in the Durham coalfield. Quarterly Journal of Engineering Geology 28, S101–S113.

Younger, P.L., 1998. Coalfield Abandonment: Geochemical Processes and Hydrochemical Products. In: Nicholson, K. (Ed.), Energy and the Environment. Geochemistry of Fossil, Nuclear and Renewable Resources. Society for Environmental Geochemistry and Health. McGregor Science, Aberdeenshire, pp. 1–29.

Younger, P.L., 2000. Nature and practical implications of heterogeneities in the geochemistry of zinc-rich, alkaline mine waters in an underground F-Pb mine in the UK. Applied Geochemistry 15, 1383–1397.

Younger, P.L., 2004. "Making water": the hydrogeological adventures of Britain's early mining engineers. In: Mather, J.D. (Ed.), 200 Years of British Hydrogeology. Geological Society, London, Special Publications, 225. pp. 121–157.

Younger, P.L., 2007. Groundwater in the Environment: An Introduction. Blackwell Publishing, Oxford 318 pp.

Younger, P.L., Manning, D.A.C., 2010. Hyper-permeable granite: lessons from test-pumping in the Eastgate Geothermal Borehole, Weardale, UK. Quarterly Journal of Engineering Geology and Hydrogeology 43, 5–10, http://dx.doi.org/10.1144/1470-9236/08-085.

Younger, P.L., 2013. Deep geothermal: the Newcastle Science Central Borehole. Geothermal Association of Ireland Newsletter 21, 9–13.

Younger, P.L., 2014. Hydrogeological challenges in a low-carbon economy (The 22nd Ineson Lecture). Quarterly Journal of Engineering Geology and Hydrogeology 47 (1), 7–27, http://dx.doi.org/10.1144/qjegh2013-063.

Younger, P.L., Milne, C.A., 1997. Hydrostratigraphy and hydrogeochemistry of the Vale of Eden, Cumbria, UK. Proceedings of the Yorkshire Geological Society 51, 349–366.

Younger, P.L., Gluyas, J.G., Stephens, W.E., 2012. Development of deep geothermal resources in the UK. Proceedings of the Institution of Civil Engineers – Energy 165 (issue EN1), 19–32, http://dx.doi.org/10.1680//ener.11.00009.

Ziegler, K., Coleman, M.L., Howarth, R.J., 2001. Palaeohydrodynamics of fluids in the Brent Group (Oseberg Field, Norwegian North Sea) from chemical and isotopic compositions of formation waters. Applied Geochemistry 16, 609–632.