Nuclear Waste Services

Guide to Reference Groundwater and Porewater Compositions in Support of the UK GDF Programme

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Preface

Nuclear Waste Services carries out geoscientific studies in support of geological disposal of the UK's higher activity radioactive waste. The work presented in this report provides a preliminary assessment of the potential chemistry of ground / pore waters present within a number of possible repository host rocks. It should be noted that this report is not exhaustive, either in respect of chemical parameters included, or in relation to geographical or geological setting. Nuclear Waste Services accepts the data and conclusions in this report.

British
Geological
Survey

Guide to Reference Groundwater and Porewater Compositions in Support of the UK GDF Programme

Geo-disposal Radwaste Programme

Open Report OR/22/001

BRITISH GEOLOGICAL SURVEY

GEO-DISPOSAL RADWASTE PROGRAMME

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Core section of Kimmeridge Clay Formation at shallow depth (137 m), North Yorkshire © UKRI, 2022

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Guide to Reference Groundwater and Porewater Compositions in Support of the UK GDF Programme

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Foreword

This reference guide has been produced by the British Geological Survey (BGS) in collaboration with Quintessa under sub-contract to Quintessa. The guide represents an output for the project RWM543 “Reference Groundwaters” which was undertaken between August 2021 and March 2022. The structure of the document is as specified by Nuclear Waste Services (NWS). This report has been produced in accordance with governance and assurance processes published in NWS’ corporate management system. All data supplied are either the prior rights of BGS or are derived from third parties, in which case the source of the data are cited.

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Summary

This guide provides a summary of available data and information relating to the chemical compositions of groundwaters/porewaters within a defined group of Lower-Strength Sedimentary Rocks (LSSRs) across England. The available data have been collated as a first step towards characterisation of the chemical compositions of water and to define realistic “reference” compositions for porewater/groundwater from the defined LSSRs. These are intended to encompass the compositional ranges likely to be encountered in a GDF construction, operational and closure context.

The LSSRs of interest in this study are defined as the Kimmeridge Clay Formation (KCF), Oxford Clay Formation (OCF), Mercia Mudstone Group (MMG) and thick evaporites within the MMG. These rock types of interest are present in localities where Nuclear Waste Services (NWS) is in formal discussion as at the date of this report with communities about the development of a geological disposal facility (GDF) for higher-activity radioactive waste for the UK.

“Credible”, internally-consistent groundwater and porewater compositions are models based on limited analytical data and caution should be applied when using them. The requirement for these credible compositions has arisen from the needs of the advancing UK GDF programme, but in the absence of specific sites or site-specific data. The intended uses of the data include technical development activities for the GDF programme, including for example radiochemistry safety assessments, materials investigations and engineering design.

Investigations of data have been made from existing national databases including pre-existing data from the published literature and BGS archives (including former Nirex studies). Summaries are also made of reference porewater compositions from suitable potential analogues from other British and overseas studies, including for English Lias, Callovo-Oxfordian Clay of Bure, East Paris Basin, France, and the Opalinus Clay from Mont Terri, Switzerland.

Investigations have highlighted that available data for groundwater/porewater from the English LSSRs are limited, reflecting both a lack of previous studies and the challenges of acquisition of reliable data. In particular, recovery of porewaters from highly consolidated clays requires lengthy procedures using bespoke apparatus, such as high-pressure squeezing cells. The investigation also highlights the strong limitations on quality of available data, with many problems associated with sampling artefacts for both collected groundwater and porewater.

Chemical compositions have been investigated for LSSRs in areas defined as the East Irish Sea Basin, east Lincolnshire, East Anglia and the Wessex Basin, to be reflective of variable rock compositions in varying hydrogeological settings and with variable evolutionary histories which are encountered across England. These areas do not reflect any preference in location for siting a GDF

At this early stage of LSSR investigations, the reference porewater/groundwater compositions are derived by a combination of lines of reasoning, including available raw data, rock mineralogy, hydrogeochemical evolutionary history and equilibrium geochemical modelling. They are not defined by real observed groundwater/porewater data, although in some cases, they may be close.

The reference waters are internally consistent, meaning that:

- values of all chemical parameters could feasibly occur together in situ in the rock;
- the composition is charge-balanced;
- the water chemistry is consistent with the mineralogy of the rock.

The reported porewater and groundwater analyses have been used as inputs to geochemical models that adjust the concentrations of certain constituents to attain internal consistency (e.g. balance charge on Cl^- concentration) and use mineral solubility constraints to fix the concentrations of aqueous constituents for which data are lacking (e.g. constrain dissolved Al concentrations by equilibrium with gibbsite and dissolved SiO_2(aq) concentrations by equilibrium with amorphous silica). The results are a reference water chemical composition in terms of the major cations and anions, total dissolved solids (TDS) and pH.

The reference porewaters/groundwaters compositions derived in this study are summarised in Section 2. The reference data provided are based on limited evidence and are not a substitute for detailed field observational data, sampled according to well-designed field experiments, which would form a next step in site-specific data gathering and investigation.

The selection of a suitable reference porewater or groundwater will depend on site-specific considerations and the intended use case (e.g., modelling, experimentation etc). It is recommended to consult an NWS Groundwater Chemistry expert before using any compositions described herein.

1 Introduction

1.1 BACKGROUND

In 2018 in England and 2019 in Wales, the Working With Communities policies were launched, which started the siting process for a Geological Disposal Facility (GDF). In readiness for the siting and construction of a GDF to accommodate higher-activity radioactive waste, NWS requires background data and evaluation on representative porewater/groundwater chemical compositions within an identified group of potential GDF host rocks present within England and Wales. Such information provides a starting point in establishing the ambient waters likely to be present in given settings.

At the time of writing, formal discussions are taking place with communities in Copeland and Allerdale in Cumbria, and Theddlethorpe in Lincolnshire. In these locations, NWS is engaging with local people about the potential for hosting a GDF in their region, including the deep geology, up to 1000 m depth and extending up to 20 km beyond the coast. This inshore area offers the potential for hosting disposal vaults and galleries beneath the seabed, whilst surface facilities and access points would be on land. In these locations, the rock types of interest can be characterised as Lower-Strength Sedimentary Rocks (LSSRs) (RWM, 2016). LSSRs are fine-grained sedimentary rocks with a high clay content[1] and, in some cases, evaporitic formations are contained within them. Potential GDF host rocks are widespread across the UK and are also present in areas other than those described in this document. This leaves the opportunity open for communities that may be interested in discussing the potential for hosting a GDF.

In order to assess the implications for design and construction, information is needed on the possible geochemical environment of a yet-to-be constructed GDF. Use of this might include interaction with engineered barrier and backfill and corrosion of materials, as well as the potential implications for radionuclide transport and wastewater management and disposal. This guide therefore considers the porewaters and groundwaters contained within LSSRs, outlining the main processes likely to be controlling them, and makes first steps towards their characterisation.

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[1] "Clay content" refers to the content of clay grade particles with sizes < 2 μm and is a broader term than "clay minerals" which refers to phyllosilicates within the < 2 μm fraction.

For the purposes of the guide, “groundwater” is defined as water free to flow by advection, provided that a head gradient exists to drive flow. Such water occupies connected macropores (>50 nm, IUPAC Gold Book). By contrast, “porewater” is dominantly immobile and may (depending on the method of extraction) include components of “free water”, water loosely in a diffuse double layer, and water more strongly bound at mineral surfaces (Pearson et al., 2003). Porewater is present in mesopores (2–50 nm, IUPAC) and micropores (<2 nm), due to the binding forces at mineral surfaces and to constricted apertures between pores. Ionic solutes and water molecules (as traced by stable oxygen and hydrogen isotopic compositions) in porewaters move primarily by diffusion through connected micropores. While the degree to which water must be bound to surfaces before it is considered a porewater is not precisely defined, the distinction between groundwater and porewater is useful in practice and is applied by radioactive waste management programmes in other countries. Environment Agency regulatory procedures are geared towards protection of “groundwater” (Environment Agency, 2018).

A “reference” water is a credible and internally consistent groundwater/porewater composition that could occur in a specified LSSR formation under given environmental and hydrogeological conditions. It is an estimate based on a combination of available water analyses for the rock formations of interest, available data for analogous formations and geochemical modelling. The geochemical modelling has been used to:

1. adjust the concentrations of certain aqueous constituents to achieve charge balance;
2. constrain the concentrations of some aqueous constituents by specifying equilibrium with minerals that occur in the rock, including cation exchangers (principally clay minerals); and
3. calculate the compositions of mixtures between different possible waters within the considered LSSR (e.g. residual depositional water and water presently in a bounding aquifer) while maintaining equilibrium with selected minerals in the rock.

The precise combination of analytical data, analogue information and geochemical model will vary depending on regional conditions, rock types and available information.

Establishing reference water for an evaporite rock unit requires slightly different considerations. It might include the composition of water that is in direct contact with the evaporite and therefore dissolving the minerals within it, as well as the composition of water in adjacent low-permeability sedimentary rock that acts as a sealing layer to reduce dissolution of the evaporite.

For each formation in each setting, there are a number of credible, consistent compositions, reflecting both heterogeneity of the formation and uncertainty in the available information. The number of presented compositions varies depending on data availability, quality and regional conditions. Several reference water compositions are given for each study area to account for a range of salinities and major-ion variations. Analogue data from other European studies have been referenced where appropriate.

1.2 SCOPE

For the purposes of developing this guide, rock formations of interest have been defined as:

- Oxford Clay Formation (OCF);
- Kimmeridge Clay Formation (KCF);
- Mercia Mudstone Group (MMG);
- Mercia Mudstone Group thick evaporite units.

These four formations span the range of LSSRs and evaporites that might be encountered in site investigations in the UK. They also align with the geological settings of communities currently considering hosting a GDF. The planning assumptions are as follows:

- Relatively simple to characterise LSSR: encompasses less complex lithologies with thick sequences of argillaceous rock dominated by clay minerals (e.g. smectite, illite, mixed-layer illite-smectite, chlorite, kaolinite); this requires less intrusive investigations to characterise (e.g. OCF);
- More complex to characterise LSSR: encompasses more complex lithologies with interbedded clastic and evaporitic strata; requires more detailed intrusive investigations to characterise (e.g. MMG).

It should be noted at the time of writing, that no decisions have been made on site selection or host rock preference. Should ongoing engagement with communities identify potential host rocks outside the current scope of this report, further work will be required to develop reference groundwaters for these host rocks.

Both the planning scenarios set out incorporate an LSSR or evaporite host rock where water and solute movement are dominantly by diffusion. In the less complex case, the formation is assumed to contain a proportion of swelling clay minerals (e.g. smectite and/or illite/smectite) such that the formation may have a self-sealing capability (NDA, 2016) and small potential for groundwater flow by advection. In the more complex case, which includes a combination of siliciclastic and evaporite lithologies, clay minerals may be a much smaller proportion of the rock and in siliciclastic and some evaporite lithologies transmissive fractures and/or more permeable beds may allow advection. In evaporitic rock types, presence of relatively soluble halite, anhydrite/gypsum and other evaporite minerals mean that brines are likely to be present.

The specified depth range of interest currently proposed for the GDF programme is 200–1000 m. In this guide, the focus of modelling is based upon the mid-range of 400–600 m in order to suitably bound the study. Due to the very limited availability of data in these ranges, groundwater/porewater compositions at shallower depths (<200 m) have also been appraised to provide some basis for assessing dominant geochemical controls and extrapolation to greater depths by inference and geochemical modelling.

The guide evaluates:

- groundwater/porewater chemical composition, focussing on major-ion concentration ranges;
- ancillary data for dating groundwater/porewater and informing water evolutionary history (e.g. isotopic compositions);
- rock physical properties to inform geochemical modelling of groundwater flow mechanisms (e.g. porosity, transport mechanism).

The chemical parameters presented in this guide are not exhaustive but were selected on the basis of prioritisation, data limitations and non-site-specific nature of the study. Further details on parameters of interest which are out of the current scope are provided in Section 3.2. Reduction-oxidation (redox) and pH conditions, organic content, and trace metals are discussed qualitatively in Sections 2.6, 2.7 and 2.8 respectively, given their particular relevance to corrosion and radionuclide mobility. Geomicrobiological aspects are not considered in this study. This needs to be recognised as a limitation of the reference groundwaters characterisation. The end products of microbial activity can have detrimental impacts on the GDF concept and this would need to be taken into account when reference waters are used for safety considerations in a GDF and engineered barrier context.

The specified spatial scope of investigation is England-wide, including an area offshore up to 20 km from the coast. In addition, four areas of the country have been identified for more detailed investigation of porewater/groundwater compositions and associated hydrogeological information in contrasting geographical and geological settings:

- East Irish Sea Basin (EISB);
- East Lincolnshire;
- East Anglia;
- Wessex Basin, southern England.

These areas are included in this study to cover a range of geological settings for the rock types of interest. They do not reflect any preference in location for siting a GDF. They were also selected on the basis of varying Quaternary glacial history, two of the areas having been impacted by (and lying north of the limit of) Devensian glaciation and two not. Three of the areas examined lie to the north of the limit of the older Anglian glaciation (Figure 1).

Figure 1. Selected study areas (EISB: East Irish Sea Basin) and approximate limit of Devensian and Anglian glaciations across England and Wales (Entwisle and Wilding, 2010) (British Geological Survey, © UKRI, 2010); study areas selected to cover a range of paleoevolutionary environments across England.

The selection of glacial limit as a criterion is on the basis of history of glacial loading and its potential impact on groundwater recharge and movement in the geological formations in the study areas. While the effects of glacial loading could extend beyond the physical extent of a glacier or ice sheet, the impacts of glacial loading on groundwater at depth may be more local.

1.3 USES OF THIS GUIDE

1.3.1 Applications

The derived reference groundwater/porewater compositions are intended to provide a first assessment of the main solutes present in deep groundwaters or porewaters in an LSSR environment and therefore likely to come into contact with the GDF. This should help to inform a range of preliminary assessments including for water management during excavation and operation of a GDF, through to informing long-term engineered barrier stability. This assists in evaluation of radionuclide and non-radioactive GDF-derived contaminant behaviour including mobilisation/retention, and planning site investigations to obtain site-specific groundwater/porewater data in a UK setting. However, it should be cautioned that perturbations to the reference condition will arise from construction activities and natural future perturbations.

The derived groundwater compositions can also provide some initial assessment of porewater/groundwater likely to be encountered during construction and an idea of unperturbed groundwater/porewater chemical characteristics for a limited suite of analytes. These data are useful for defining initial conditions for predictive geochemical simulations.

This guide is not intended to provide a comprehensive account of pre-development baseline conditions in ambient porewater/groundwater. It is addressed towards engineers, designers, safety specialists, modellers and geoscientists who are involved with the early phases of developing a UK-based facility before data are available from intrusive site-specific investigations.

Derived reference compositions are inevitably uncertain owing to the use of limited quantities of data, data of uncertain quality, analogue data from shallower depths and other formations and the application of geochemical models, which are inevitably simplifications of the real world. Compared to surface conditions, those at 400–600 m involve greater pressures and higher temperatures than evident at shallower depths (average UK geothermal gradient of 26°C/km (Busby, 2015), differing redox conditions and most likely greater solute concentrations due to enhanced residence time, geochemical reactions (especially of evaporites) and mixing with older generations of saline water that have not previously been flushed under the conditions of low hydraulic conductivity and gradients. Geochemical modelling itself carries inherent uncertainties in determining input parameters, controlling geochemical reactions, need for consideration of microbially mediated reactions, and kinetic and thermodynamic data, especially for any considered minor and trace elements and for certain minerals.

The limitations of the derived reference data approach mean that the reference compositions are not a substitute for good-quality, site-specific observational chemical data. These latter would be needed in the early exploratory stages of GDF development for the purposes of verifying the nature of solutes in contact with GDF components, as well as for wastewater disposal and baseline characterisation. Parameters such as Sr, U, Ra and Th for establishing geochemical baselines and isotopes ($^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{4}He/^{3}He$, ^{14}C, ^{3}H) which are relevant to groundwater fingerprinting require site specific data and are therefore not evaluated in the current study.

To relate the reference groundwater/porewater compositions derived in this guide to other water types, compositions of major ions in waters from a range of different origins are given in Table 1. Compositions include a fresh Chalk groundwater (Shand et al., 2007), seawater (from Hem, 1992), a hypersaline (higher salt content than seawater) brine from a deep well in the Sherwood Sandstone Group at Southampton (Allen et al., 1983) and a hypersaline brine from Sherwood Sandstone having interacted with halite from Permian Zechstein deposits at the Boulby Mine, Cleveland (Bottrell et al., 1996).

Table 1. Examples of solute compositions for fresh, potable Chalk groundwater (drinking water), open seawater, and brines from a deep well in Sherwood Sandstone (Western Esplanade, Southampton) (Allen et al., 1983) and British hypersaline brine (Bottrell et al., 1996) (concentrations in mg/L; SEC: specific electrical conductance in mS/cm).

Water type	pH	TDS	SEC	Ca	Mg	Na	K	Cl	SO_4	NO_3	HCO_3
Potable Chalk groundwater	7.4	290	0.5	90.8	1.57	9.70	0.77	22.3	21.9	40.3	204
Seawater	8.1	35,000	50	410	1350	10,500	390	19,000	2700	3.0	142
Deep brine	6.0	124,000	155	4240	752	41,300	705	75,900	1230	nd	71
Halite-contacted brine	6.9	204,000	-	1290	452	79,000	624	118,000	3100	nd	153

nd: not detected.

1.3.2 How to use

The information contained within this guide is intended to be used to underpin decisions regarding initial state of groundwater chemistry during the early stages of the GDF programme, in the absence of site-specific data. Reference compositions are designed such that they cover a range of LSSR/evaporitic geological settings at GDF-relevant depths, and cover what is considered to be a credible range of conditions that may be expected in host-rock porewaters. Reference water chemical compositions are provided in Section 2. Section 3 provides details of the study methodology, geological and hydrogeological settings, data and assessment of data quality.

Table 2. Summary of reference waters for lithologies within settings studied as set out in Section 2. Numerical references are provided to sections discussing and presenting data, with "RW" denotations highlighting the relevant reference waters. End Members (EM) and Boundary Waters (BW) used in the derivation of reference waters are also recorded in Table 3. More information on how the reference waters were derived is presented in Section 2 and Appendix 4.

	Mercia Mudstone Group (MMG)	Massive Evaporite, MMG	Kimmeridge Clay (KCF)	Oxford Clay (OCF)
East Irish Sea Basin (EISB)	**Section** 2.2.2 (RW1–12)	**Section** 2.2.3 (RW13–14)		
	EM1, EM2, BW1, BW2	EM1, EM2		
East Lincolnshire	**Section** 2.3.2 (RW15–20)		**Section** 2.3.3 (RW21–24)	**Section** 2.3.4 (RW25–28)
	EM1, EM2, BW3		EM3, BW4	EM4, BW5
East Anglia	**Section** 2.4.2 (RW29)			
	EM5			
Wessex Basin			**Section** 2.5.2 (RW30–31)	**Section** 2.5.3 (RW32)
			EM6	EM7

In Section 2, the reference waters are split into regions which vary by setting and paleo-evolutionary history: East Irish Sea Basin (EISB); East Lincolnshire; East Anglia and Wessex Basin, where the rock types studied are present at depth ranges of interest for a GDF. The guide then sets out each of the four rock types in these settings, including the MMG, MMG Evaporites, KCF and OCF, as explained by Table 2. Reference waters are provided for a range of mixtures of end members for each of these rock types and settings. The end members approximate old formation waters and waters from bounding strata, such that the reference groundwaters provide a credible range of compositions which may arise from mixing of these waters in the deep subsurface. As a result, a large number of “credible reference waters” are provided in tabulated form in each subsection, which covers a realistic range of conditions across multiple lithologies and regions.

For a particular field of application selection of a reference groundwater/porewater, or range of reference compositions, from among those supplied in this guide should be based upon expert judgement relevant to the field. For example, the parameters to which a specific process is most sensitive should be considered, in order to ensure adoption of a conservative approach. In most cases, it is advised that the full range of conditions presented is considered for any given use, in order to capture the uncertainty surrounding these data. Individual reference waters presented are internally consistent, such that they should be used in their entirety; please refer to Section 3.5 for further details.

As the GDF programme progresses, some reference data presented in this guide may become redundant, for instance where there are no longer any interested communities where a specific rock type is present. Conversely, where new interested communities enter the programme, with new rock types of interest, further work will be required to extend the scope of this guide. It is notable that, whilst a massive evaporite is considered within the MMG, these data should not be used to represent massive evaporites elsewhere. After future borehole drilling and sampling, reference waters will be developed further, based on site-specific conditions.

2 Reference water compositions

2.1 INTRODUCTION

This section provides the primary output of this study: modelled reference water compositions for preliminary application in the UK GDF programme. Suites of waters are provided which cover a realistic range of credible conditions, for each geological unit of study in the selected basins studied. The reference waters have been derived from geochemical modelling including where appropriate, mixing calculations, based on evidence gathered and presented in Section 3. These reference compositions are intended to be an early evidence base to inform future GDF design and prompt site investigation and further modelling. The compositions deemed most appropriate for further consideration will depend on the objective of enquiry and potential location (rock type, geography and depth) of a future GDF.

As will be discussed further in Section 3.5, the LSSRs considered in this report are typically bounded by aquifers, and the water compositions at the margins of these LSSR formations are likely to be comparable to those found presently in the aquifers. On the other hand, the porewater at the centre of each formation of interest is most likely to be close to original depositional water. Between the centre of a considered LSSR and its margins, the porewater will be a mixture between the waters lying at these locations. The proportion of bounding aquifer water will increase towards the margin of the LSSR.

2.2 EAST IRISH SEA BASIN

2.2.1 Approach to deriving reference water compositions for the EISB

The modelling methodology used to derive reference water compositions is described in Section 3.5. The way in which this methodology was used to derive credible reference water compositions for the MMG in the EISB is as follows:

- The “removal” of fresh water from a deep brine pumped from the Sherwood Sandstone Group at a depth of 1100 m in Sellafield borehole BH3 (see Table 18) was modelled until reaching halite saturation, while keeping the brine in equilibrium with selected minerals (halite, anhydrite, calcite, dolomite) in the rock (based on Section 3.6.4.2). The rationale is that the salinity in this BH3 brine is believed to have originated predominantly in the evaporites of the MMG, and been diluted by mixing with meteoric water (Bath et al., 2006); the modelling effectively simulates the reversal of this mixing process to derive the most saline water composition possible. The resulting water composition was considered as one credible MMG Reference Water composition and is labelled EM1 (End Member) in Table 3 and Table 4.

- A reported composition of Agden Brine, pumped from the MMG at a depth of 150 m in the Mersey Basin (see Table 17) was modelled to assess whether it is saturated/oversaturated/undersaturated with halite and to ensure internal consistency. It was confirmed that the composition is at near-saturation with halite, hence it is considered as another credible MMG reference water composition and is labelled EM2 in Table 3 and Table 4.

- The composition of groundwater pumped from the Sherwood Sandstone Group at a depth of 206 m in Sellafield borehole BH2 (Bath et al., 2006) is fresher water considered to be of a type that could either have contacted the lower boundary of the MMG in the past, or potentially could do so in the future, during periods of low sea level. If water of the kind sampled from 206 m in BH2 were to contact the MMG it would mix with more saline in-situ water (either EM1 or EM2, calculated as described above). It should be noted that any fresh water of meteoric origin that might in future come into contact with the upper boundary of the MMG, in periods of low sea level, would likely have a composition broadly similar to this BH2 water. This BH2 composition is labelled BW1 (Boundary Water) in Table 3.

- Standard seawater (Millero et al., 2008) is considered to be another water type that potentially could penetrate the MMG and mix with more saline in-situ water (either EM1 or EM2, calculated as described above). About 1.5 km offshore from Sellafield the MMG comes close to the seabed (it is mostly overlain by a thin layer of unconsolidated sediments) and hence is clearly in contact with seawater. This seawater composition is labelled BW2 in Table 3.

Based on the above-mentioned assumptions, a set of mixing calculations was completed to derive credible water compositions in the MMG, while maintaining equilibrium with in-situ minerals of the rock (based on Section 3.6.4.2). The halite-saturated brine composition calculated by “removing” water from the Sellafield borehole BH3 composition was also saturated with respect to anhydrite and dolomite, while Al and Si contents were constrained by equilibrium with gibbsite and amorphous silica respectively. The same mineral equilibria constraints were placed on Al and Si concentrations of the Sellafield borehole BH2 water (Bath et al., 2006) and marine waters (Millero et al., 2008). In addition, these latter two waters were specified to be in equilibrium with calcite and anhydrite. These two minerals were kept in equilibrium throughout the mixing calculations.

All the geochemical models were produced using the PHREEQC v 3.7.1.15876 software and the thermodynamic database THEREDA 2020 release (Moog et al., 2015). This database was chosen because it was developed specially for application to radioactive waste disposal following well-documented procedures and with a high degree of testing. Further details are given in Section 3.5.

Full details of the model constraints are given in the PHREEQC input files provided in Appendix 4.

2.2.2 Mercia Mudstone Group (MMG)

A set of credible reference water compositions for the MMG are shown in Table 3. These compositions were calculated by assuming equilibrium with several minerals, as described in Section 2.2.1. Each reference water was specified to contain a different amount of boundary water i.e. 10%, 50%, and 90%. These different mixing proportions are provided to give an indication as to how the water composition might vary between the centre of the formation (lower proportion of boundary water) and the formation’s boundary (higher proportion of boundary water).

The mineral equilibrium constraints specified when modelling these compositions are described in Section 2.2.1. For more information on trace elements, see Section 2.8.

Table 3. Credible reference water compositions for the Mercia Mudstone Group (MMG) in the East Irish Sea Basin (EISB), covering a range of potential mixing ratios; concentrations in mg/L.

	RW1*	RW2	RW3	RW4	RW5	RW6	RW7	RW8	RW9	RW10	RW11	RW12
	EM1[#] + BW1[~]			EM1 + BW2			EM2 + BW1			EM2 + BW2		
	10%^	50%	90%	10%	50%	90%	10%	50%	90%	10%	50%	90%
TDS	291,612	174,796	41,423	294,178	189,191	71,740	288,776	173,034	40,987	291,392	187,566	71,382
Ca	1963	2527	1867	1903	2287	1965	1306	2141	1772	1261	1939	1891
Mg	1069	628	141	1185	1236	1290	373	222	55	490	834	1206
Na	110,225	64,271	13,504	111,094	69,090	23,106	111,012	64,692	13,585	111,877	69,511	23,187
K	510	298	64	546	488	423	95	56	13	132	247	373
HCO_3	110	118	117	108	104	91	243	200	135	241	187	109
SO_4	2899	4985	4231	2919	5272	6075	4538	5926	4394	4591	6291	6284
Cl	174,847	101,947	21,413	176,434	110,697	38,719	171,225	99,779	20,946	172,818	108,543	38,262
SiO_2(aq)	35	58	100	34	55	89	36	60	100	35	56	89
Al	1	0.01	0.003	1	0.01	0.004	3	0.02	0.003	2.8	0.03	0.004
pH	6.1	6.5	6.9	6.1	6.5	7.0	6.0	6.4	6.9	6.0	6.4	6.9

*RW – Reference Water; [#]EM – End Member; [~]BW – Boundary Water (e.g. from bounding aquifers); ^the amount of Boundary Water in the mixture.

2.2.3 Mercia Mudstone Group (MMG) evaporites

A set of credible reference water compositions for the MMG evaporites is shown in Table 4. These compositions were calculated by assuming equilibrium with several minerals, as described in Section 2.2.1. For more information on trace elements, see Section 2.8, where it is explained that aqueous concentrations of Al in porewaters are expected to be very low (as shown for EM1). However, the estimated Al concentration is sensitive to the assumptions made about the identity of the buffering mineral phase and the initial pH, which for EM2 results in higher values of Al compared to EM1.

Table 4. Credible reference water compositions for the Mercia Mudstone Group (MMG) evaporites in the East Irish Sea Basin (EISB); concentrations in mg/L.

	RW13*	RW14
	EM1#	EM2
TDS	319,436	317,403
Ca	1797	1222
Mg	1174	410
Na	121,193	122,261
K	561	105
HCO_3	81	135
SO_4	2368	4673
Cl	192,216	188,572
SiO_2(aq)	95	31
Al	0.01	24
pH	5.9	5.8

*RW – Reference Water; #EM – End Member.

2.3 EAST LINCOLNSHIRE

2.3.1 Approach to deriving reference water compositions for East Lincolnshire

The modelling methodology used to derive reference water compositions is described in Section 3.5. The ways in which this methodology was used to derive credible reference water compositions for the MMG, the KCF, and the OCF present in East Lincolnshire are as follows.

The approach for the MMG was as follows:

- Water pumped from the Sherwood Sandstone Group aquifer at the Welton location (see Table 22) was considered to be a potential less saline water type that could be penetrating the MMG (BW3). This boundary water would then be mixing with more saline in-situ water, which was assumed to originate predominantly in the evaporites of the MMG (labelled as EM1 and EM2 in Table 4). Equilibrium with in-situ minerals of the rock was maintained, following the same approach as for MMG described in Section 2.2.1.

The approach for the KCF was as follows:

- Modelling involved equilibration between standard seawater (composition from Millero et al., 2008) and selected minerals in the rock (kaolinite, quartz, calcite, pyrite, dolomite, muscovite), adopted from Section 3.6.2.2. Ion-exchange equilibria were also considered, using cation-exchange capacities reported by Gillespie et al. (2000) (mean value of 30.82 meq/100g for the KCF using a $BaCl_2$ method) and assuming porosity of

4% and density of 2000 kg/m^3 (Section 3.7). Cation-exchange capacity was also estimated from the proportions of minerals in the rock and values for minerals reported in Appelo and Postma (2007). These were in good agreement, but due to inherent variability of minerals within any given rock (as shown in Section 3.6.2.2), the Gillespie et al. (2000) mean cation-exchange capacity was used. Following Parkhurst and Appelo (2013), equilibrium constants for Na^+, K^+, Ca^{2+} and Mg^{2+} were adopted as 0, 0.7, 0.8 and 0.6, respectively. The resulting water composition was considered to be a credible porewater composition and is labelled EM3 in Table 6.

- Water from the Spilsby Sandstone aquifer (Table 22) was considered as a potential freshwater type that could be penetrating the KCF and mixing with in-situ water (EM3). The Spilsby Sandstone aquifer water was considered to be a credible boundary water and its composition is labelled BW4 in Table 6. During the mixing calculations, the same mineral and ion-exchange equilibria were considered as those described above.

The approach for the OCF was as follows:

- Modelling involved equilibration between standard seawater (Millero et al., 2008) and selected minerals in the rock (kaolinite, quartz, calcite, pyrite, siderite, gypsum), adopted from Section 3.6.3.2. Ion-exchange equilibria were also considered, using cation-exchange capacities estimated in Gillespie et al. (2000). The same approach as for the KCF was followed (as explained earlier). The resulting water was considered to have a credible reference composition for a porewater and is labelled EM4 in Table 6.

- As OCF is located stratigraphically below the KCF, the water composition on the boundary of the OCF was determined by mixing the model KCF porewater (EM3 in Table 6) and boundary water from the Spilsby Sandstone (BW4 in Table 6) in the proportion 1:1; the resulting composition is labelled BW5 in Table 7. Such credible boundary water (BW5) was then mixed with the OCF water (EM4 in Table 7). During the mixing calculations, the same mineral and ion-exchange equilibria were considered as those described above for the KCF.

Based on the above-mentioned approaches, a set of mixing calculations was completed to derive credible reference water compositions in the MMG, the KCF, and the OCF, while maintaining equilibrium with those in-situ minerals in the rocks of interest considered plausibly to approach equilibrium. In addition, for the KCF and the OCF, ion-exchange equilibria were considered.

The modelling used PHREEQC v 3.7.1.15876 software and the thermodynamic databases Thermochimie v 10a (Giffaut et al., 2014) and THEREDA 2020 release (Moog et al., 2015) were used for the KCF and OCF, and for the MMG, respectively. These databases were chosen because they were developed specially for application to radioactive waste disposal following well-documented procedures and with a high degree of testing. Further details are given in Section 3.5.

Full details of the model constraints are given in the PHREEQC input files provided in Appendix 4.

2.3.2 Mercia Mudstone Group (MMG)

A set of credible reference water compositions for the MMG in East Lincolnshire is given in Table 5. These compositions were calculated according to the approach described in Section 2.3.1. Each specified reference water contains a different proportion of boundary water i.e. 10%, 50%, and 90%. These different mixing proportions are provided to give an indication as to how the water composition might vary between the centre of the formation (lower proportion of boundary water) and the formation's boundary (higher proportion of boundary water). For more information on trace elements, see Section 2.8.

Table 5. Credible reference water compositions for the Mercia Mudstone Group (MMG) in the East Lincolnshire area; concentrations in mg/L.

	RW15*	RW16	RW17	RW18	RW19	RW20
	EM1# + BW3~			EM2 + BW3		
	10%^	50%	90%	10%	50%	90%
TDS	292,166	177,840	47,884	289,300	176,012	47,414
Ca	1990	2662	2247	1322	2254	2142
Mg	1094	759	389	399	354	304
Na	110,381	65,143	15,264	111,167	65,567	15,345
K	513	315	96	99	73	46
HCO_3	106	93	69	238	176	87
SO_4	2843	4682	3956	4457	5566	4092
Cl	175,250	104,165	25,778	171,635	102,004	25,314
SiO_2(aq)	35	58	97	36	59	97
Al	1	0.01	0.004	3	0.02	0.003
pH	6.1	6.5	7.0	6.0	6.4	6.9

*RW – Reference Water; #EM – End Member; ~BW – Boundary Water (e.g. from bounding aquifers); ^The amount of Boundary Water in the mixture.

2.3.3 Kimmeridge Clay Formation (KCF)

A set of credible reference water compositions for the KCF in East Lincolnshire is given in Table 6. Reference waters RW22, RW23 and RW24 each contain a different proportion of water from the boundary i.e. 10%, 50%, and 90%. These different mixing proportions are provided to give an indication as to how the water composition might vary between the centre of the formation (lower proportion of boundary water) and the formation's boundary (higher proportion of boundary water). These compositions were calculated according to the approach described in Section 2.3.1. For more information on trace elements, see Section 2.8.

As mentioned earlier, the OCF is located stratigraphically below the KCF. Hence, the differences in the porewater composition between the two rocks are driven predominantly by the differences in mineralogy. For instance, the apparent high value of Ca in the KCF porewater (EM3 in Table 6) is due to the presence of dolomite (as adopted from Table 12). However, the data in Table 12 for dolomite come from an offshore area, and the reference compositions provided in Table 6 might differ from the compositions found in an onshore area, stemming from potential differences in mineralogy. Nevertheless, the values outlined in Table 6 provide a range of credible compositions. Alternative compositions for both KCF and OCF are given in Section 2.5.

Table 6. Credible reference water compositions for the Kimmeridge Clay Formation (KCF) in the East Lincolnshire area; concentrations in mg/L.

	RW21*	RW22	RW23	RW24
	EM3#	EM3 + BW4~		
		10%^	50%	90%
TDS	36,147	32,660	18,865	5,165
Ca	1443	1229	497	41
Mg	817	679	244	17
Na	10,966	10,069	6227	1757
K	55	51	30	8
HCO_3	437	442	484	844
SO_4	2758	2487	1422	348
Cl	19,722	17,753	10,000	2176
SiO_2(aq)	9	9	10	11
Al	2.1E-05	2.0E-05	2E-05	5E-05
pH	6.2	6.2	6.4	7.0

*RW – Reference Water; #EM – End Member; ~BW – Boundary Water (e.g. from bounding aquifers); ^the amount of Boundary Water in the mixture.

2.3.4 Oxford Clay Formation (OCF)

A set of credible reference water compositions for the OCF in East Lincolnshire is given in Table 7. Each of the reference waters RW26, RW27 and RW28 contains a different proportion of boundary water i.e. 10%, 50%, and 90%. These different mixing proportions are provided to give an indication as to how the water composition might vary between the centre of the formation (lower proportion of boundary water) and the formation's boundary (higher proportion of boundary water).

The reference water compositions were calculated according to the approach described in Section 2.3.1. For more information on trace elements, see Section 2.8.

Table 7. Credible reference water compositions for the Oxford Clay Formation (OCF) in the East Lincolnshire area; concentrations in mg/L.

	RW25*	RW26	RW27	RW28
	EM4#	EM4 + BW5~		
		10%^	50%	90%
TDS	36,135	34,680	29,102	23,500
Ca	544	519	436	366
Mg	1306	1216	892	613
Na	10,968	10,556	8939	7228
K	406	391	329	264
HCO_3	85	133	311	482
SO_4	3102	3160	3380	3636
Cl	19,726	18,708	14,829	10,937
SiO_2(aq)	9	9	10	10
Al	5E-05	4E-05	3E-05	3E-05
pH	7.1	6.9	6.7	6.6

*RW – Reference Water; #EM – End Member; ~BW – Boundary Water (e.g. from bounding aquifers); ^The amount of Boundary Water in the mixture.

2.4 EAST ANGLIA

2.4.1 Approach to deriving reference water compositions for East Anglia

Due to the availability of water composition data for the depth of interest in the MMG in East Anglia, the water composition reported in Table 23 is considered as a credible reference water composition. However, to adjust the reported water composition and make it internally consistent, a partial equilibrium model was developed, taking into account the mineralogy of the rock. The reported water (EM5) composition was assumed to be in equilibrium with anhydrite and calcite, while Al and Si contents were constrained by equilibrium with gibbsite and amorphous silica respectively. For the modelling the PHREEQC v 3.7.1.15876 software and the thermodynamic database THEREDA 2020 release (Moog et al., 2015) were used. This database was chosen because it was developed specially for application to radioactive waste disposal following well-documented procedures and with a high degree of testing. Further details are given in Section 3.5.

Full details of the model constraints are given in the PHREEQC input file provided in Appendix 4.

2.4.2 Mercia Mudstone Group (MMG)

A credible reference water composition for the MMG in East Anglia is given in Table 8.This composition was derived as described in Section 2.4.1. Alternative credible reference water compositions for the MMG can be selected from Table 3 and Table 5. For more information on trace elements, see Section 2.8.

Table 8. Credible reference water compositions for the Mercia Mudstone Group (MMG) in the East Anglia; concentrations in mg/L.

	RW29*
	EM5$^{\#}$
TDS	57,542
Ca	3873
Mg	798
Na	16,661
K	239
HCO_3	166
SO_4	2741
Cl	32,996
SiO_2(aq)	92
Al	0.01
pH	6.4

*RW – Reference Water; $^{\#}$EM – End Member.

2.5 WESSEX BASIN

2.5.1 Approach to deriving reference water compositions for the Wessex Basin

Due to the lack of water composition data for the depth of interest in the KCF in the Wessex Basin, the water compositions reported in Table 25 for a location at Ashdown (east Sussex) are considered as credible reference water compositions. These data are from the Weald Basin, which can be considered an extension of the Wessex Basin. However, to adjust the reported water compositions and make them internally consistent, a partial equilibrium model was developed, taking into account the mineralogy of the rock. The reported water compositions were assumed to be in equilibrium with kaolinite, quartz, calcite, pyrite, dolomite and muscovite, while Al and Si contents were constrained by equilibrium with gibbsite and amorphous silica respectively.

Due to the paucity of data for water compositions in OCF in the area of interest, data from a borehole in Didcot, Oxfordshire was used (Table 26). An alternative would have been to use the water composition from the Harwell No. 4 borehole, but this has a very high sulphate content and low pH, possibly indicative of pyrite oxidation related to sampling. Consequently, this sample was not used. To adjust the water composition reported for Didcot and make it internally consistent, a partial equilibrium model was developed, taking into account the mineralogy of the rock. The reported water composition (EM7) was assumed to be in equilibrium with kaolinite, quartz, calcite, pyrite, siderite, and gypsum, while Al and Si contents were constrained by equilibrium with gibbsite and amorphous silica respectively

For the modelling PHREEQC v 3.7.1.15876 software and the thermodynamic database Thermochimie v 10a (Giffaut et al., 2014) were used. This database was chosen because it was developed specially for application to radioactive waste disposal following well documented procedures and with a high degree of testing.

Further details are given in Section 3.5. Full details of the model constraints are given in the PHREEQC input files provided in Appendix 4.

2.5.2 Kimmeridge Clay Formation (KCF)

A set of credible reference water compositions for the KCF in the Wessex Basin is given in Table 9. The water compositions were derived as described in 2.5.1. For more information on trace elements, see Section 2.8.

Table 9. Credible reference water compositions for the Kimmeridge Clay Formation (KCF) in the Wessex Basin; concentrations in mg/L.

	RW30*	RW31
	EM6$^{\#}$	
TDS	35,721	23,321
Ca	170	67
Mg	103	36
Na	13,484	8,806
K	18	11
HCO_3	642	868
SO_4	780	591
Cl	20,559	12,975
SiO_2(aq)	9	10
Al	3E-05	4E-05
pH	6.6	6.8

*RW – Reference Water; $^{\#}$EM – End Member.

2.5.3 Oxford Clay Formation (OCF)

A credible reference water composition for the OCF in the Wessex Basin is given in Table 10. The water composition was derived as described in Section 2.5.1. Alternative credible reference water compositions for the OCF can be selected from Table 7. For more information on trace elements, see Section 2.8.

Table 10. Credible reference water composition for the Oxford Clay Formation (OCF) in the Wessex Basin; concentrations in mg/L.

	RW32*
	EM7#
TDS	9,891
Ca	402
Mg	205
Na	2858
K	73
HCO_3	186
SO_4	1785
Cl	4,383
$SiO_2(aq)$	10
Al	4E-05
pH	6.9

*RW – Reference Water; #EM – End Member.

2.6 REDOX AND pH CONDITIONS

The pH and redox state of a groundwater or porewater, as represented by redox potential (Eh), are key parameters. While most of the water analyses that have been obtained for this study include pH measurements (Section 3.8), Eh data are very few. For the reasons explained in subsequent paragraphs, the pH and Eh data are likely to be perturbed from in-situ values to some extent, particularly in the case of Eh measurements. Indeed, reported Eh values are invariably of questionable reliability.

The pH and Eh of a water need to be known to determine the state of equilibrium / disequilibrium between the water and mineral assemblage in a rock. Depending on the nature of a solute, these parameters may affect its solubility significantly. The pH and / or Eh of water may significantly control the distribution of the solute among different dissolved chemical species (e.g. the distribution of dissolved Fe between Fe^{2+} and Fe^{3+}). Over the ranges of pH and Eh that are credible for LSSR or evaporites, some dissolved elements will not change speciation significantly. However, water-mineral systems are complex coupled systems. Therefore, even if the speciation of a particular dissolved element on its own would change little over relevant ranges of pH and Eh, there may be pH and / or Eh-dependent changes in the chemical speciation of the element if it can form complexes with species of other dissolved elements that are pH- and/or Eh-dependent. For example, dissolved Ca might be expected to occur dominantly in the form of Ca^{2+} in dilute $CaCl_2$ solutions. The speciation of Ca^{2+} would change little over wide ranges of pH and Eh. However, Ca^{2+} may form complexes with dissolved HCO_3^- (dominant at 25 °C and $6.1 < pH < 10.1$) or CO_3^{2-} (dominant at greater pH). The species $CaHCO_3^+$ might be dominant at 25 °C and $5.1 < pH < 8.1$, while $CaCO_3^0$ would be dominant at greater pH.

Measured values of pH and Eh in-situ in a deep borehole, in water sampled from a borehole, or in porewater extracted from rock cored from a deep borehole will inevitably be perturbed to some degree from in-situ values. This is particularly the case for Eh, which is readily disturbed by contamination with atmospheric oxygen. Oxidation of sulphide minerals may significantly reduce the measured pH compared to in-situ values, as well as perturbing Eh. Contamination of in-situ waters by drilling fluids, corrosion of drilling equipment, and degassing of CO_2 during sampling are among other important processes that may perturb Eh and pH.

An additional factor is that an Eh value is a measured electrode potential that depends on the concentrations of oxidised and reduced species interacting with the electrode. However, it needs to be borne in mind that redox disequilibria are common in nature. Generally, redox reactions involving transfer of more electrons are slower than those involving transfer of fewer electrons. Thus, oxidised and reduced aqueous S-species (SO_4^{2-} and HS^-) are less likely to be in equilibrium than oxidised and reduced aqueous Fe-species (Fe^{2+} and Fe^{3+}). If disequilibria occur, a consequence is so-called “mixed” electrode potentials, which will not represent in-situ conditions. A complicating factor is that microbial activity may increase the rates of these reactions and perturb the measured potentials.

To account for the processes that may perturb measured Eh and pH, it is necessary to use geochemical modelling to correct measured values, as far as possible. To do this requires an assumption of redox and pH equilibrium between dissolved species in the water and minerals in the rock. For example, an Eh value can be calculated if chemical equilibrium is assumed and the rock contains pyrite and siderite, and analyses of coexisting water include values for pH, SO_4 concentration and inorganic carbon (HCO_3) concentration. However, the assumption of in-situ equilibrium may not be correct and/or, for a given rock and coexisting water analysis, there will be more than one credible set of redox and / or pH – controlling mineral-solute equilibria. Thus, generally a range of credible pH and Eh will need to be specified based on alternative equilibrium assumptions. The significance of these ranges will need to be explored in sensitivity calculations.

Several lines of evidence point towards reduced (anoxic and substantially negative Eh) in the considered potential GDF host rock types:

- the occurrence of minerals containing reduced forms of elements such as Fe (e.g. siderite, pyrite) which in principle could interact with any oxygen present and produce reducing conditions;

- the low permeability of the rocks, which means that contained porewater and groundwater will have a very long residence time (favouring an approach to redox equilibrium with reduced minerals);

- the great depths (> 200 m), which contributes to isolating the rock from the atmosphere; and

- in-situ studies in LSSR at sites in other countries, such as the Jurassic Callovo-Oxfordian rocks at Bure in France (Gaucher et al., 2006) and Jurassic Opalinus Clay at Mont Terri Tunnel in Switzerland (Pearson et al., 2003), which have demonstrated reducing conditions.

However, site-specific investigations in the host rock of any future GDF site will need to demonstrate such reducing conditions.

The pH and Eh ranges reported in published literature for several rock types that are mineralogically similar to one or more of the LSSR and evaporites considered here, are given in Table 11.

Table 11. Examples of ranges of pH and Eh in rocks with some similarities to the LSSR and evaporites considered in the present study.

Rock Formation	pH range	Eh range (mV)	Source
Opalinus Clay, Mont Terri	7.2 to 8.5	-283 to -50	Pearson et al. (2003)
Callovo-Oxfordian, Bure	7.1 to 7.4	-176 to -200	Gaucher et al. (2006)
Sherwood Sandstone Group, Southampton	6.0 to 6.8	-300 to -200	Downing et al. (1983)
Sherwood Sandstone Group, Sellafield	6.5 to 7.8	No reliable data	Nirex (1997)

2.7 ORGANIC CONTENT

Dissolved organic compounds may be an important component of porewaters in some of the considered rock formations. Some of the rocks may also contain discrete organic phases, gas and / or petroleum liquids, although these are outside the scope of this report which concerns the compositions of waters.

Some of the organic compounds will potentially be able to form complexes with radionuclides. However, there are very few data available for the organic contents of porewaters in the considered rock formations in the considered areas. Such data that do exist are total organic carbon (TOC) concentrations or dissolved organic carbon (DOC) concentrations[2] and there are no details of the nature of the organic materials. However, the limited available data suggest that TOC contents in the OCF and KCF would likely be a few 10's of mg/L (see Table 19 and Table 29). For comparison, similar concentrations of TOC have been reported for the Opalinus Clay in Switzerland (Pearson et al., 2003; the largest value reported was 448 mg/L).

It is expected that there will be a general relationship between the organic content of the rock and the organic content of the porewater; higher organic contents in the rock will likely result in higher organic contents in the porewater. However, the precise relationship will be complex since the ability of the solid organic matter in the rock to contribute aqueous organic solutes to the porewater will depend on the nature of the organic matter and its degree of maturity at the time the porewater enters the rock. Reflecting their respective organic matter contents, it is expected that the porewaters in the OCF and KCF will tend to have higher TOC contents than the porewaters in the MMG. Halite dominated evaporite sequences generally have very low organic contents and TOC concentrations in porewaters will be very low.

2.8 TRACE ELEMENTS

2.8.1 Data availability

Trace-element data are largely unavailable for the rock formations considered. Such data are inherently harder to obtain from LSSR and evaporites than data for major and minor constituents, owing to the low concentrations at which the trace elements occur. These low concentrations make trace elements particularly susceptible to contamination and other perturbing processes during sampling and analysis. Many of them are redox-sensitive and in such cases, unless water samples can be extracted and analysed without contacting the atmosphere, measured concentrations will differ from in-situ values. Therefore, at this early

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[2] TOC usually refers to all the organic carbon in an unfiltered sample, whereas DOC refers to the organic carbon in a sample filtered to e.g. 0.45 μm.

stage of investigations, estimates need to be made based on mineral equilibrium assumptions and analogue information from other sites. In the case of evaporites, the typical very high porewater salinities make analysing trace constituents difficult owing to matrix effects. Samples need to be diluted substantially to make analysis feasible, with the result that concentrations of some trace elements may be reduced below their detection limits. In the sections below, controls on the concentrations of important trace constituents (Al, Fe, HS^-, heavy metals) are discussed and indicative credible concentrations are given where feasible.

2.8.2 Al concentrations

Aqueous concentrations of Al in porewaters are expected to be very low, typically between 10^{-10} mol/kg and 10^{-7} mol/kg over the range of pH that is relevant to most natural LSSR porewaters (pH 5–8.5). However, the estimated Al concentration is sensitive to the assumptions that are made about the identity of the buffering mineral phase. In LSSRs of the kinds considered in this project, dissolved Al concentrations are most likely to lie between values buffered by kaolinite and values buffered by gibbsite (Figure 2). Pearson et al. (2003) concluded that in the Opalinus Clay, the former was most likely to buffer aqueous Al concentrations, based partly on the occurrence of kaolinite in the Opalinus Clay. However, kaolinite is not ubiquitous in the considered LSSRs.

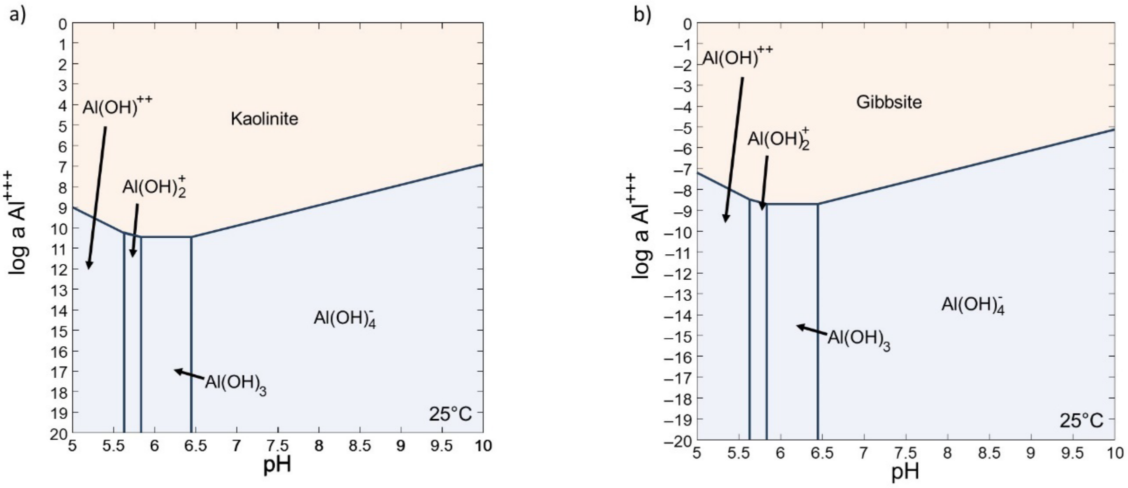

Figure 2. Solubility plots for a) kaolinite ($Al_2Si_2O_5(OH)_4$) and b) gibbsite ($Al(OH)_3$) at 25°C, assuming that dissolved silica is buffered by amorphous silica in the case of kaolinite. “a Al” refers to “activity of Al”, numerically approximately Al concentration in mol/kg. Both diagrams were produced using Geochemist’s Workbench (GWB) and the Thermochimie v 10a thermodynamic database (Giffaut et al., 2014).

2.8.3 Fe concentrations

Like Al, Fe is also an important constituent of several minerals that occur in the considered LSSR. Estimates of aqueous Fe concentration depend on the assumed pH, the assumed solubility-controlling phase and assumptions made about controls on the aqueous concentrations of constituents of the phases other than Fe. Unlike for Al, redox conditions are also an important control on Fe concentrations, but it can be assumed that under natural in-situ conditions in a GDF host rock conditions will be reducing and Fe(II) will be the dominant form of aqueous Fe.

Figure 3 presents solubility diagrams for four candidate phases that might control Fe solubility under reducing conditions. One of these is the Fe(II) hydroxide $Fe(OH)_2$(cr) (Figure 3a). An alternative oxide phase is the Fe(III) oxide hematite (Fe_2O_3). The solubility of this latter phase depends on the assumptions or constraints concerning redox conditions (Eh). However, for credible reducing Eh, Fe_2O_3 solubility would imply lower aqueous Fe(II) concentrations than

$Fe(OH)_2(cr)$. For the redox assumptions made here, at neutral pH (7) Fe_2O_3 solubility would imply an aqueous Fe concentration of about $10^{-3.5}$ mol/kg, whereas $Fe(OH)_2(cr)$ solubility would imply an aqueous Fe concentration of about $10^{-1.5}$ mol/kg.

Another candidate phase that might control aqueous Fe solubility under reducing conditions is siderite ($FeCO_3$). Its solubility depends on the assumptions made about aqueous carbonate concentrations. However, assuming that these are controlled by a log fCO_2 of -2.5, where fCO2 is the fugacity of CO_2, a thermodynamic pressure in bar. This log fCO_2 is similar to values estimated for the Opalinus Clay (Pearson et al. (2003). Between pH = 7.5 and pH = 9.5 Fe(II) solubility would be about 10^{-5} mol/kg, while at neutral pH (7) Fe(II) solubility would be similar to that implied by Fe_2O_3 equilibrium (Figure 3b).

In some mudrocks, the activity of porewater Fe may also be controlled by equilibria with Fe-bearing phyllosilicate phases, such as Fe-chlorite (Bryndzia and Villegas, 2020). Numerous phyllosilicate phases could potentially control aqueous Fe concentrations and probably such a phase would be a solid solution rather than a pure Fe-bearing end-member. Assumptions have to be made about controls on the aqueous concentrations of other constituents of these phases besides Fe in order to calculate their solubilities. However, here for illustrative purposes the solubility of the pure Fe-bearing chlorite endmember chamosite ($Fe_5Al_2Si_3O_{10}(OH)_8$) is calculated, assuming that aqueous Si is controlled by equilibrium with amorphous silica and aqueous Al is controlled by equilibrium with gibbsite (Figure 3c). At any pH Fe(II) concentrations controlled by this phase would be several orders of magnitude lower than those controlled by the other considered phases. For example, at neutral pH (7) the solubility of chamosite would be around 10^{-6} mol/kg, whereas the solubility of hematite would be around $10^{-3.5}$ mol/kg (assuming Eh -0.3V), the solubility of siderite would be similar to that of hematite, and the solubility of $Fe(OH)_2(cr)$ would be around $10^{-1.5}$ mol/kg.

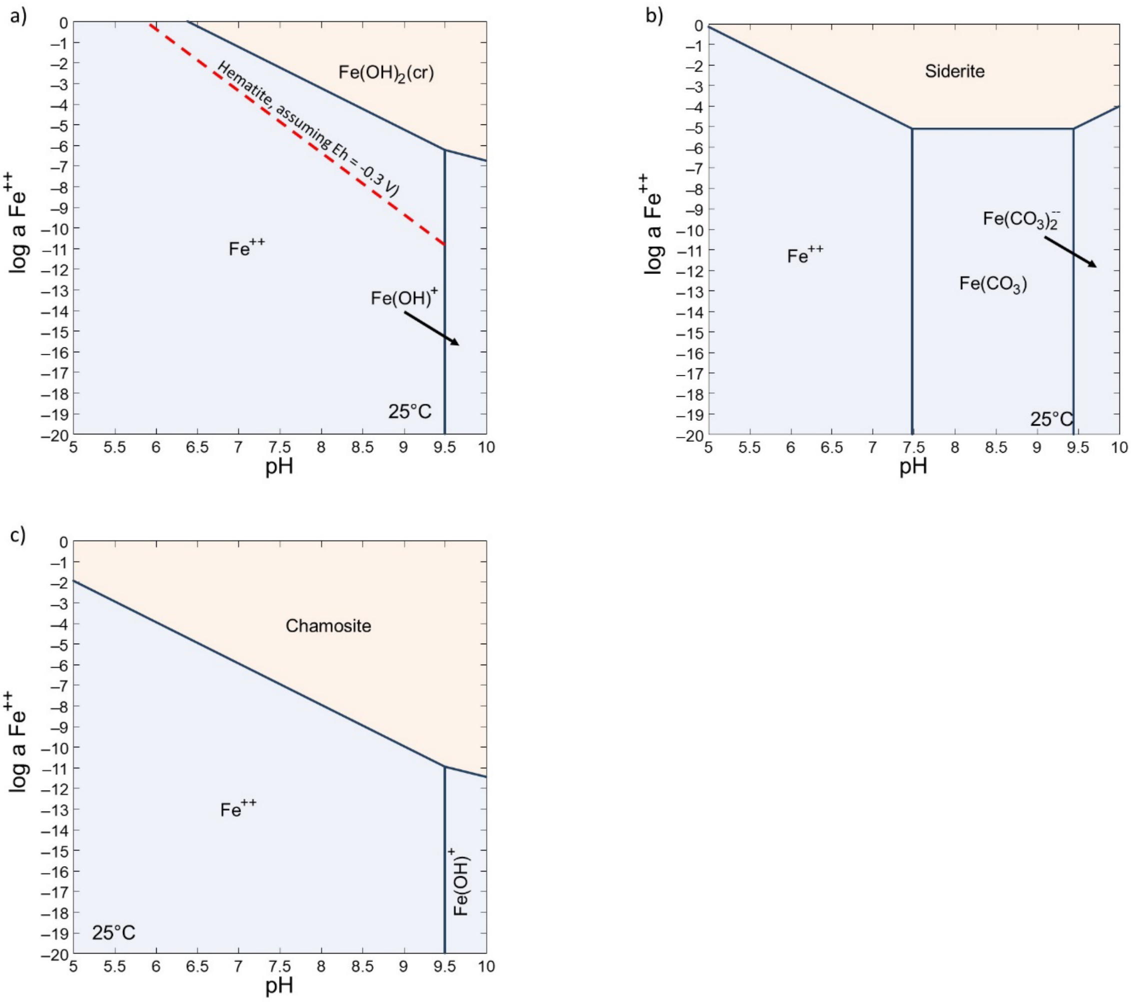

Figure 3. Solubility plots showing the solubility of Fe assuming different mineral buffers: a) $Fe(OH)_2$(cr) and hematite (Fe_2O_3 assuming Eh = -0.3V, left); b) siderite ($FeCO_3$, assuming log fCO_2 = -2.5 b); fCO_2 is the fugacity of CO_2 approximately the partial pressure of CO_2); and c) Chamosite, an Fe-chlorite ($Fe_5Al_2Si_3O_{10}(OH)_8$), assuming also that aqueous Al is controlled by equilibrium with gibbsite ($Al(OH)_3$) and aqueous Si is controlled by equilibrium with amorphous silica (SiO_2,am). “a Fe” refers to “activity of Fe”, numerically approximately Fe concentration in mol/kg. All diagrams were produced using The Geochemist’s Workbench (GWB) and Thermochimie v 10a thermodynamic database (Giffaut et al., 2014).

2.8.4 Sulphide concentrations

Dissolved sulphide is a potentially significant influence on corrosion of certain metals that might be emplaced in a GDF. It is therefore desirable to estimate concentrations of dissolved sulphide in porewaters. However, no data are available for the considered rock formations. Furthermore, in-situ sulphide concentrations are very difficult to determine owing to the ease with which sulphide is oxidised on exposure to the air, which is very difficult to avoid during core sampling, porewater extraction and analysis.

In the considered rocks the most common mineral that might buffer aqueous sulphide concentrations is pyrite (FeS_2). However, the solubility of this phase (and hence aqueous sulphide concentrations) is coupled to reactions that buffer aqueous Fe concentrations. As explained in Section 2.8.3, a number of mineral phases could be involved in buffering these Fe concentrations and various assumptions need to be made to calculate Fe concentrations that are controlled by a given buffer (e.g. fCO_2, approximately the partial pressure of CO_2, and pH need to be assumed if an Fe concentration consistent with siderite equilibrium is to be calculated). A further complicating factor is that sulphide participates in microbially-mediated reactions that may also involve organic matter.

For these reasons, there is considerable uncertainty about the likely in-situ aqueous sulphide concentrations within the considered rock formations. For illustrative purposes, Figure 4 shows the stability of selected mineral phases that may participate in buffering aqueous sulphide concentrations, in Eh – log a S^{2-} space, for several different assumptions about Fe concentration, pH and fCO_2. These diagrams show that dissolved sulphide concentrations could range through many orders of magnitude, but all are very low; the highest concentration among the illustrated cases is about 10^{-9} mol/kg. For comparison, Pearson et al. (2003) considered that the in-situ aqueous sulphide in the Opalinus Clay is most likely buffered by siderite and pyrite and calculated concentrations of c. 10^{-11} mol/kg.

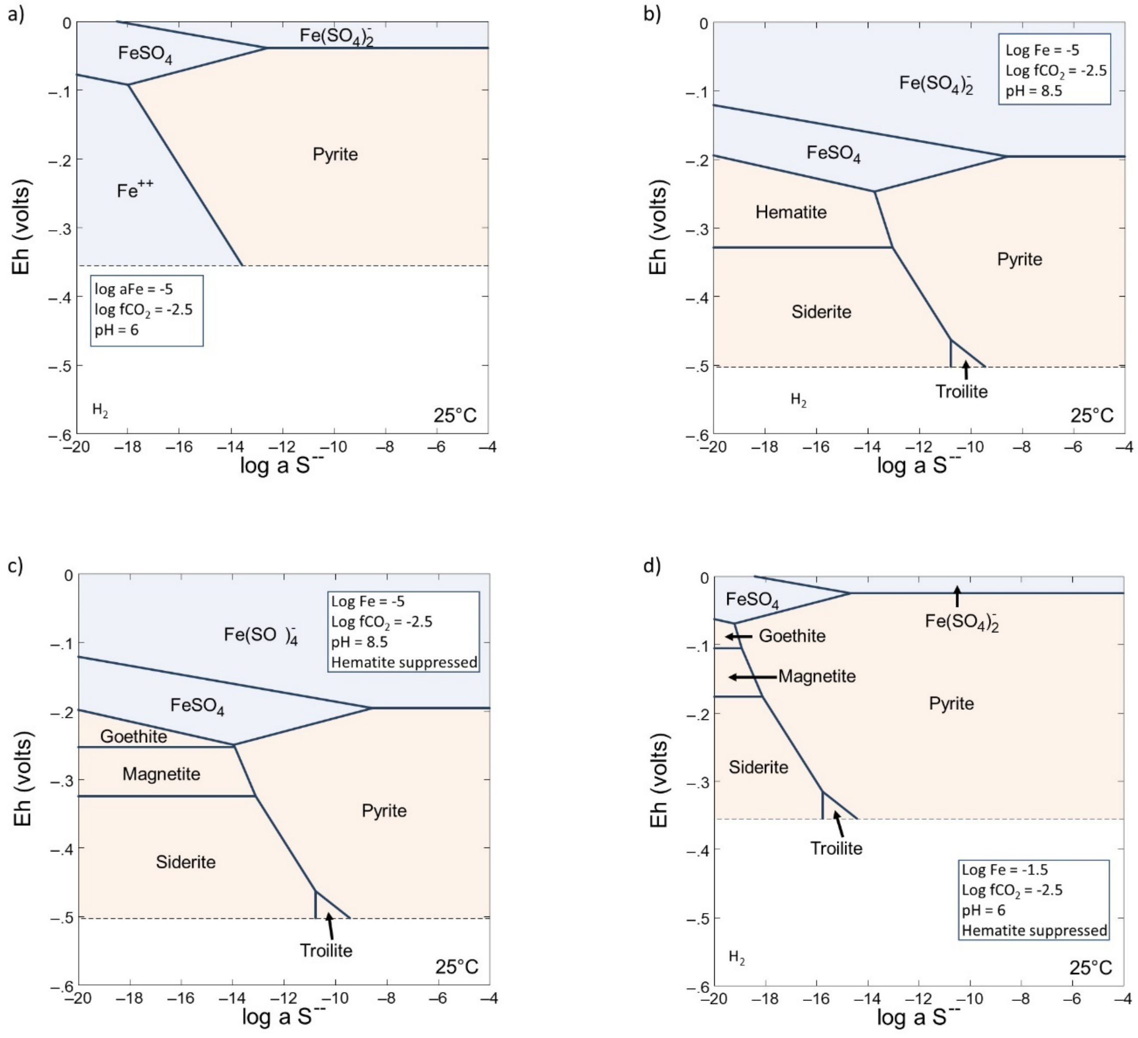

Figure 4. Plots showing the stability fields of selected minerals that potentially could buffer dissolved sulphide concentrations in the porewaters of LSSR, shown in Eh- log aS^{--} space. Various assumptions are made concerning Fe activities, pH and stable minerals, as shown in the diagrams. “a S^{--}” refers to “activity of S^{--}”, numerically approximately S^{--}concentration in mol/kg. Pyrite = FeS_2; Troilite = FeS; Siderite = $FeCO_3$; Hematite = Fe_2O_3; Goethite = FeO(OH). All diagrams were produced using The Geochemist’s Workbench (GWB) and Thermochimie v 10a thermodynamic database (Giffaut et al., 2014).

2.8.5 Heavy-metal concentrations

The concentrations of many heavy metals that occur in the porewater of LSSR and evaporites in principle could be estimated by modelling using a mineral-equilibrium constraint, in a similar way to modelling the concentrations of Al and Fe as described above. Equilibrium models could be implemented easily by using PHREEQC together with input files modified from those given in Appendix 4. Trace elements of interest and appropriate mineral-equilibrium constraints can be added to these input files. However, identifying appropriate mineral constraints is often not straightforward. Related to this problem is the fact that many trace elements are not essential constituents of solid phases in the rocks, but rather occur as trace constituents of one or more phases; thermodynamic data to model mineral solubilities are typically available only for pure phases. The incorporation of trace elements in solids may depend on precipitation kinetics. Furthermore, sorption processes on clay surfaces also regulate trace-element concentrations. While approaches are available to model release of such minerals, thermodynamic data to use in such models may not be available. It may also be impractical to take into account incongruent trace-element release from solid phases which may occur. A further issue for brines, such as those found typically in halite-dominated evaporites, is that the Pitzer approach to thermodynamic modelling is required. However, thermodynamic data to allow this approach to be applied are lacking for many trace elements. Hence, at this step of the approach, the trace elements are not derived.

2.9 SUMMARY

For a number of years, the UK programme has operated in a “generic” space, without remit to focus upon specific rock types. Much work and learning to date has therefore relied on overseas programmes, particularly France, Switzerland and Belgium with respect to repository development in clay host rocks. This study advances UK knowledge with respect to porewater conditions in potential English LSSRs, providing insight into variability between lithologies here and overseas. The study has investigated potential controls on the compositions of high-salinity waters (brines) in LSSR sequences that contain evaporites (i.e. the MMG). Any future activities to develop a GDF in such LSSR will need to consider how these high-salinity waters may interact with engineered barriers. It is noteworthy that little research has been undertaken in other countries on potential sedimentary repository host rocks that contain brines, but which are not evaporites.

Figure 5 provides a high-level summary of porewater chemistries for selected reference waters from the UK. In order to highlight the variation between major overseas programmes, these porewater chemistries are then compared to the values reported in the major overseas programmes (see Table 1 and Section 3.8.6) in the following text.

The concentrations of both the Na and Cl ions within the MMG are generally an order of magnitude higher than in the OCF and KCF. These concentrations range from 13,000 mg/L at the lower-range depth of key relevance, close to the mixing point with fresh waters on the boundary, to 110,000 mg/L for solutions expected at the mid-range depth of key relevance (around 400–600 m). Concentrated solutions up to 190,000 mg/L are expected for halite-dominated sequences and where mixing with fresh groundwater is negligible. Concentrations of those ions in the MMG are about one and two orders of magnitude higher in comparison with the data for Opalinus Clay in Switzerland and the Callovo-Oxfordian clays in France, respectively.

While the SO_4 concentrations for all three LSSRs of interest are generally within the same order of magnitude, i.e. ranging between 1500 mg/L and 6000 mg/L, lower concentrations (350–800 mg/L) can be expected for the KCF at the lower-range depth of key relevance (e.g. 200 m), which is close to the mixing point with freshwaters on the boundary. The SO_4

concentrations in the waters of Opalinus and Callovo-Oxfordian clays are comparable to the values estimated for the LSSRs of interest.

The concentrations of both the Ca and Mg ions in the KCF and OCF are comparable to the concentrations found in the waters of Opalinus and Callovo-Oxfordian clays, and range between 50 mg/L and 1500 mg/L. However, the variability in the concentrations is most pronounced for the KCF, especially in the East Lincolnshire area. Although the Mg concentration in the MMG is comparable to other LSSRs of interest, as well as to the data from overseas programmes, the concentration of Ca is higher, with concentrations in the range of 1200–3900 mg/L.

The waters of MMG and OCF share comparable concentrations of HCO_3 (80–250 mg/L and 80–480 mg/L respectively). This is also comparable to the values reported from overseas programmes. Conversely, the concentration of HCO_3 in the KCF is somewhat higher, i.e. 400–850 mg/L.

The variability in K concentrations for all three LSSRs of interest is consistent with the values reported from the overseas programmes. However, it is credible that higher concentrations of K are to be found in the MMG (up to 550 mg/L) and the OCF (up to 400 mg/L) compared to the KCF (up to 55 mg/L). The concentrations of $SiO_{2(aq)}$ are expected to be low (i.e. ca. 10 mg/L) in the Jurassic clays, which accords with the data from overseas programmes. However, the $SiO_{2(aq)}$ concentrations in the MMG are an order of magnitude higher, i.e. up to 100 mg/L.

There are few or no data available for TOC, DOC, Al, Fe, sulphide or heavy metal concentrations in the porewaters of the considered rock formations. Based on the limited data and information from similar formations in other countries, TOC concentrations are likely to be a few tens of mg/L. For Al, Fe, sulphide and heavy metals, concentrations depend strongly on the nature of buffering mineral assemblages and calculated equilibrium values may vary widely depending on the assumptions that are made. Al concentrations are likely to be very low (a reasonable range is 2.5×10^{-6} mg/L to 2.5×10^{-3} mg/L). Fe concentrations are also likely to be low, most likely ca. 0.5 mg/L. Aqueous sulphide concentrations are most likely to be ca. 10^{-7} mg/L.

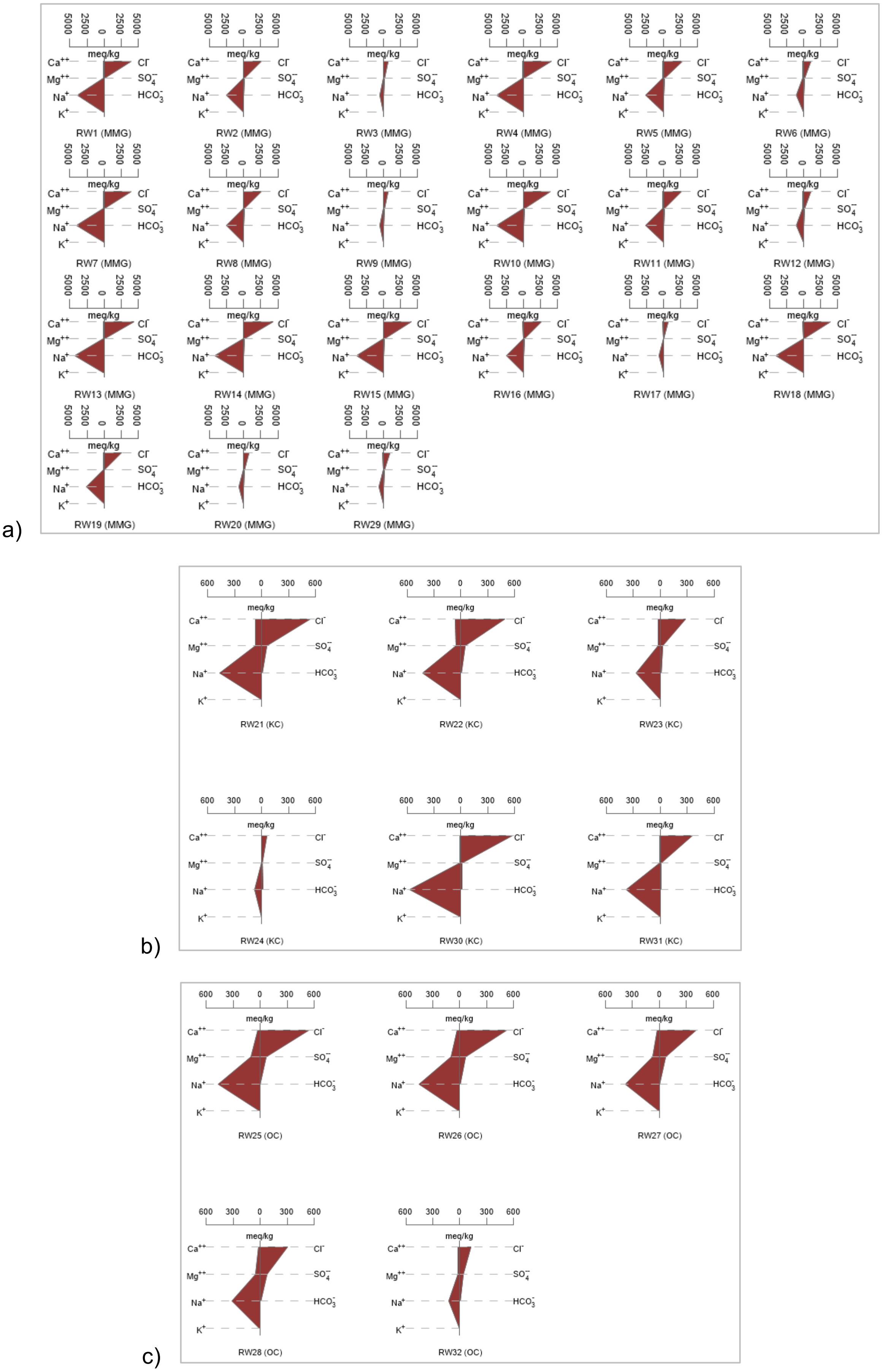

Figure 5. Summary of three reference waters for UK LSSRs: a) Mercia Mudstone Group (MMG), including the evaporite sequence (values taken from Table 3, Table 4, Table 5, and Table 8); b) Kimmeridge Clay Formation (KCF) (values taken from Table 6 and Table 9); c) Oxford Clay Formation (OCF) (values taken from Table 7 and Table 10).

3 Methodology

3.1 INTRODUCTION

This section provides information on activities carried out to collate data for the purposes of carrying out the geochemical modelling described in Section 2 and compiling the guide. It outlines the background to the spatial distributions and stratigraphical relationships of the rock types of interest, their mineralogy and evolutionary history. Collated data for observed water chemistry from the chosen rock types are described, along with details of sampling methodology and measurement uncertainties. The chemical data are also provided.

3.2 WORKSHOPS

Activities involved set up of two workshops which were held to understand stakeholder needs and seek feedback on approach and direction. The first workshop was held in September 2021 and involved Quintessa, BGS, Intellisci and members of the steering group (comprising experts from Golder, Galson, University of Bern and Nuclear Waste Services; see Acknowledgements). This established the parameters for investigation (confirming which analytes in water, minerals, hydraulic properties should be included) and finalised the rock types of interest, study areas and approach. An extensive list of parameters was identified for consideration in this study. However, the non-site-specific nature of the reference waters and, limitations of data availability, mean that the focus was placed on major cations and anions. This approach provides critical information to a wide range of users and facilitated a robust approach to geochemical modelling, including calculation of charge balance. Key parameters that will be relevant but not presented for reference waters include:

- minor and trace constituents, mainly transition metals as well as Br, Ba, Sr, U, Ra and Th for establishing geochemical baselines;
- humic or dissolved organic compounds (e.g., acetate) that can influence radionuclide mobility through the formation of colloids and ionic complexes;
- isotope (e.g., $\delta^{18}O$, δD, $^{87}Sr/^{86}Sr$ and $^{3}He/^{4}He$) and element (e.g., Br/Cl) ratios that provide information on the provenance (e.g., meteoric, marine and hydrothermal) of ground and porewaters;
- isotope abundances that can be used for groundwater dating (e.g., ^{3}H, ^{14}C, ^{39}Ar, ^{36}Cl, ^{81}Kr and ^{85}Kr);
- dissolved gases (CH_4, H_2S and Rn) for analytical purposes and to understand possible hazards during construction.

A second workshop was held with the steering group in November 2021 to consult on research direction and to help shape the contents of the reference guide.

3.3 GEOLOGY COLLATION

The spatial extent of the LSSRs and evaporite for four study areas as specified at the first workshop and by consultation with NWS stakeholders, was established through compilation of BGS onshore and offshore 3D digital geological data and available lithostratigraphic borehole logs. Due to the distribution of identified offshore boreholes, the search area was extended to some 25 km offshore. The rock types of interest have also been modelled in the four areas identified for more detailed investigation.

3.4 GROUNDWATER/POREWATER CHEMISTRY COLLATION

3.4.1 Data search methodology

Searches of hydrogeochemical data have accessed:

- published literature (via Web of Science searches);
- commissioned reports (e.g. Nirex, BGS reports);
- BGS database of squeezed porewater and groundwater data;
- hydrogeochemical data stored on BGS Wellmaster (groundwater borehole records);
- hydrogeochemical data stored in offshore lithological logs;
- relevant hydrogeochemical data evaluated from analogue studies (e.g. international clay porewaters, information from adjacent aquifers).

In addition, ancillary data from the above sources have been collated for the four study regions for:

- groundwater/porewater isotopic data for assessing fluid history;
- rock physical properties;
- LSSR/evaporite mineralogy.

Porewaters collated in this guide may have been extracted by clay squeezing under air or nitrogen gas, or in some cases by centrifugation. In the cases of both groundwater samples and porewater samples, many processes during sampling can perturb the analysed groundwater chemistry. For example, in pumped or bailed groundwater, samples may be contaminated by drilling fluid, may have reacted with drilling equipment, and may be impacted by artefacts of squeezing. Rock sampled for porewater squeezing may also have been contaminated by drilling fluid. In groundwater sampled by bailing or pumping to surface, or porewater extracted in air, samples are highly vulnerable to changes in redox conditions (oxidation) and CO_2 losses (perturbation of pH and carbonate equilibria) post-extraction. Even in porewater extracted under nitrogen, some oxidation can take place. In all samples analysed at surface, temperatures are susceptible to influence by ambient atmospheric temperature. All these limitations have been evaluated in Section 3.8 for the collated observational data. Details of the consideration of groundwater/porewater data confidence, with colour coding to give a qualitative assessment, are given in Appendix 3. All depths referred to in this guide are vertical depths.

3.4.2 Confidence in groundwater/porewater chemical compositions

Compositions of porewaters and groundwaters in LSSRs at the depth ranges of interest are difficult to estimate because of the paucity of observational data and variations in hydrogeological setting, lithology, sediment evolutionary history and chemical reactions that make variation likely. For example, there remains uncertainty around the nature of water (i.e. groundwater vs. porewater) within rocks such as the MMG, which are highly indurated and potentially capable of sustaining open fractures. Where observations are available, estimating compositions may be difficult depending on the methods of sampling and potential for disturbance of samples from natural in-situ conditions, although even small amounts of data at the depth ranges of interest can be extremely valuable.

Obtaining representative samples of groundwater is difficult from open wells intersecting argillaceous rocks with low hydraulic conductivity, especially at large depths (>200 m). Installation of zone-isolating packers in deep boreholes is carried out rarely due to cost. Bailing of groundwater from boreholes is likely to be more feasible, especially by mechanised methods for raising and lowering the bailer in deep boreholes. However, bailing of groundwater samples from long-screened or open boreholes risks sampling of standing water or groundwater that is otherwise unrepresentative.

A more reliable method for extracting porewaters from clay rocks, developed in BGS based on earlier USGS equipment (Brightman et al., 1985), involves squeezing core sections at high pressures (Entwisle et al., 1989). Other techniques such as aqueous extraction, diffusive exchange, leaching or vacuum distillation (Mazurek and de Haller, 2017) have not been applied in British studies due to lack of focus on LSSR rocks for geological disposal since the 1980s. Nonetheless, improvements in methodologies for the physicochemical analysis of porewaters in clays have been made in relation to geological disposal programmes elsewhere (Tournassat et al., 2015).

Potential problems of representativeness of squeezing methods have been observed from membrane effects such as ion filtering and anion exclusion and mineral reactions (Bath et al., 2001; Brightman et al., 1985; Fernández et al., 2013), as well as cation exchange (Mazurek et al., 2015). Reduced concentrations of Cl in squeezed porewater with increasing pressure can be a result of closing pore throat sizes and/or as a result of anion exclusion at clay surfaces (Gaucher et al., 2009). Variations over time in squeezed compositions have also raised questions over the relative contributions of free water from pore spaces and that adsorbed in the clay double layer (Gaucher et al., 2006). Restricting squeezing pressure appears to be a factor in ensuring extraction of free porewater alone and in limiting membrane effects (Fernández et al., 2013). Threshold squeezing pressures depend on mineralogy, pore-space configurations and degree of consolidation (Mazurek et al., 2015).

In addition, comparisons between porewater and groundwater compositions at a given site have sometimes found higher SO_4 concentrations in squeezed porewaters, typically as a result of increased pyrite oxidation during squeezing (Pearson et al., 2011).

Drillcore sampling of clay rocks may result in alteration from in-situ conditions. Changes can arise especially due to instability of parameters such as temperature, pH, redox potential and dissolved oxygen (DO). Anaerobic groundwater/porewater samples can become oxidised unless rigorous procedures are in place to minimise this, for example by using a flow cell to measure Eh and DO in pumped groundwater or extraction of porewaters in a N_2 atmosphere. Changes in physico-chemical conditions as a function of sampling disturbance, for example influx of atmospheric oxygen, can also render solutes unrepresentative due to redox changes, including oxidation of reduced solids such as organic matter or pyrite, as well as degassing and/or mineral precipitation. Data reported for the UK groundwater/porewater should therefore be treated with caution in the absence of adequate knowledge of and confidence in the methodology used for sampling, the likely perturbation of unstable parameters, and the feasibility of adjusting raw data to in-situ values. A commentary on sampling procedures is provided alongside data in this report, where information exists.

Sampling issues notwithstanding, some generalised inferences on what are reasonable porewater/groundwater compositions can be made, considering that waters in potential host rocks at the centre of the depth range of interest (200–1000 m) have been remote from sources of fresh recharging water over long periods, have had long residence times in the host rocks and may be mixed with older saline waters which are usually present at depth.

Low-permeability clay rocks at depth (>200 m) will most likely be anoxic with dissolved oxygen absent (undetected). Electrochemical potentials i.e. redox potentials for groundwater/porewater should be reducing to strongly reducing with Eh values typically well below 0 mV. Whether conditions are sufficiently reducing for SO_4 reduction or methanogenesis will depend on the nature of the lithologies and biogeochemical conditions. Such conditions are more likely in the organic-rich marine deposits (e.g. KCF, OCF) that provide the redox drivers for these reactions than the MMG hosts, but methane (CH_4) and dissolved sulphide (HS^-) may still be present. Interactions of groundwater with evaporitic formations mean the porewaters will likely be saline or hypersaline, and presence of old formation waters in deep LSSRs will also result in increased salinity.

Measurements of temperature are unreliable if not measured in situ, for example by downhole logging or hydrogeological testing. Temperature estimates can be made from the sample depth in relation to the geothermal gradient, particularly in low-permeability formations where advective flow from depth is unlikely. Given an average UK geothermal gradient of 26°C/km (Busby, 2015), a likely groundwater temperature at the depth mid-point (500 m) might be inferred around 23°C, although this will vary regionally.

3.5 GEOCHEMICAL MODELLING

It is important to ensure that the reference porewater compositions are internally consistent and include credible concentrations for some constituents that generally lack reliable analytical data, notably Al and SiO_2(aq). Here, internal consistency means that:

- values of all chemical parameters could feasibly occur together in situ in the rock;
- the composition is charge-balanced;
- the water chemistry is consistent with the mineralogy of the rock.

An example where chemical parameters for a water could not feasibly occur together in situ in the rock is a combination of measured pH, Ca concentration and inorganic carbon concentration that implies calcite to be unrealistically supersaturated, such that it would precipitate. This situation would suggest that analysed Ca and/or inorganic carbon concentrations are too high for the determined pH, or conversely that the determined pH is too high for the analysed Ca and / or inorganic carbon.

A water composition is not charge-balanced when the sum of the charge on the cations in solution (+) is not numerically the same as the sum of the charge on the anions in solution (-). This situation can arise when an analysis is incomplete (i.e. missing concentrations of some constituents), or when the analysed concentration(s) of one (or more) constituent(s) is (are) inaccurate. A measured value of pH and/or Eh that is inaccurate may also lead to a charge imbalance by affecting the calculated concentrations of anions and cations. For example, dissolved inorganic carbon at pH greater than ca. 9 is predominantly in the form of divalent CO_3^{2-}, but at lower pH, predominantly in the form of monovalent HCO_3^-. Therefore, if the real pH is a little lower than ca. 9, but the measured pH is erroneously a little greater than 9, the model will compute more negative charge in the water than in fact is the case; the water will have a negative charge imbalance.

An inconsistency between an analysed water composition and the mineralogy of the rock could arise if the measured chemical parameters indicate that a particular mineral constituent of the rock is sufficiently[3] undersaturated to dissolve. Conversely, it would also be inconsistent for an analysed water composition to be sufficiently supersatured with respect to a mineral that it would be expected to precipitate in the rock. Either of these situations would imply that the rock mineralogy would be evolving unrealistically.

To avoid these kinds of inconsistency, the reported porewater and groundwater analyses for the considered rock formations have not been used as reference porewater compositions. Instead, these analyses have been used as inputs to geochemical models that adjust the concentrations of certain constituents to attain internal consistency (e.g. balance charge on Cl^- concentration) and use mineral solubility constraints to fix the concentrations of aqueous constituents for which data are lacking (e.g. constrain dissolved Al concentrations by equilibrium with gibbsite and dissolved SiO_2(aq) concentrations by equilibrium with amorphous silica). Where mineral equilibria have been used in this way to constrain aqueous solute concentrations, the minerals have been chosen to give credible concentrations, based on a

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[3] It should be noted that some mineral precipitation and dissolution reactions occur very slowly so that some degree of calculated supersaturation or undersaturation for a particular water with respect to a given mineral will often be consistent with the rock mineralogy

large body of published research into low-temperature water-rock reactions (e.g. Oelkers and Schott, 2018 and references therein).

The models have been developed using the widely used, public-domain PHREEQC v 3.7.1.15876 software (Parkhurst and Appelo, 2013). This software was used together with thermodynamic databases Thermochimie v 10a (Giffaut et al., 2014) and THEREDA 2020 release (Moog et al., 2015). The first of these thermodynamic databases is used for Jurassic clays (OCF and KCF), whereas the latter is used for halite-bearing sequences (MMG). These databases were chosen because they were developed specially for application to radioactive waste disposal following well documented procedures and with a high degree of testing. Thermochimie is developed by an international consortium of radioactive waste management organisations, consisting of ANDRA (French National Radioactive Waste Management Agency), NWS (Nuclear Waste Services, UK) and Ondraf/Niras (National Agency for Radioactive Waste Management, Belgium). THEREDA is developed by a consortium of respected German and Swiss research organisations following the same approaches as used for development of the NEA-OECD thermochemical database. Given the early stage of LSSR investigations being undertaken by NWS, which means that uncertainties in underlying porewater and groundwater chemical compositions are large, the chosen thermodynamic databases are considered to be valid, based on the published information about them. Further validation and benchmarking are outside the scope of this project.

In all simulations, temperature was kept at 25°C, based on the information given in Section 3.4.2. All the inputs used in the modelling are reproduced in Appendix 4. For each model, details are provided of the origin of the water analyses on which the model is based and the approach to simulating in-situ conditions. The reader can copy text representing a given model from Appendix 4 and paste it into a PHREEQC input file, modify the input if required, select an appropriate thermodynamic database, and then run it.

Four types of hydrogeochemical calculation models are used:

- Type 1: speciation models to assess whether reported water compositions for a given rock formation are saturated/oversaturated/undersaturated with minerals in the rock (at in-situ temperature), which are a precursor to Type 2 models;
- Type 2: partial equilibrium models, in which some of the aqueous constituents of the water have been constrained by specifying equilibrium with minerals in the rock, to ensure that the water chemistry and mineralogy are consistent, and Cl^-, Ca^{2+}, Na^+ or inorganic carbon species (depending on the model) is adjusted to achieve charge balance;
- Type 3: models to calculate theoretical in-situ water compositions, assuming an initial depositional porewater composition and equilibrium with selected minerals in the rock, again charge balancing with either Cl^-, Ca^{2+}, Na^+ or inorganic carbon species; and
- Type 4: mixing models to calculate the compositions of mixtures between waters in the centre of a low-permeability rock formation of interest (MMG, OCF or KCF), and water on the boundary of the rock formation, while maintaining equilibrium with selected minerals in the rock (the waters that are mixed having been output by models of Type 2 or Type 3).

A Type 2 model was used to simulate the water composition that would arise by “concentrating” a water sampled by Nirex from the Sherwood Sandstone Group at 1106 m depth in BH3 drilled near Sellafield (Bath et al., 2006), until saturation with halite. The calculated composition was then used as one reference water for the MMG. The rationale is that the salinity in this water is believed to originate predominantly in the evaporites of the MMG (Bath et al., 2006), but has been diluted by mixing with fresher water within the Sherwood Sandstone Group aquifer. The model aims to reverse the effects of this dilution to obtain an estimate of the water composition in the MMG.

Type 3 models included simulation of partial equilibration between present mean seawater and OCF and between present mean seawater and KCF. Here, “partial equilibrium” means that mineral solubility controls were specified for some aqueous constituents, but not all. The choice of solubility controls was based on an assessment of which aqueous species are likely to equilibrate with solid phases. Inevitably some degree of expert judgment was needed here, though the chosen constraints are commonly used in the geochemical literature. The mean seawater composition was obtained from Millero et al. (2008). The rationale is that both these rock formations are marine and therefore the original porewater in them must have been seawater. An underlying assumption is that the composition of this water is approximately the same as present mean seawater, noting that seawater composition has varied somewhat over time (Holland, 2005). During diagenesis, there would have been chemical modification of this water, which is approximated by the partial equilibration with minerals in the rock. Owing to the very low permeabilities of the OCF and the KCF, it is credible that such chemically modified primary depositional water (connate water) is still present in places.

For the KCF and OCF, cation exchange was also considered as a control on the concentrations of some constituents (Na, K, Ca, Mg). To do this, assumptions were required to be made about which solid phases participate in ion exchange, and selectivity coefficients describing the cation exchange on each one. In the absence of porewater analyses, corresponding mineralogical data, and measured concentrations of exchangeable cations on the solid phases, there is uncertainty about the nature of the exchanging phases and the values of the selectivity coefficients to be used.

When modelling the porewater in the Opalinus Clay at Mont Terri Tunnel, Pearson et al. (2003) used generic selectivity coefficients from Parkhurst and Appelo (1999). Use of these coefficients was justified partly by the finding that the calculated porewater compositions were less sensitive to the selectivity coefficients used than the measured cation populations on the exchanger. While recognising that multiple exchangers are likely involved, in view of limited data Pearson et al. (2003) also considered the Opalinus Clay to behave as a single exchanging solid phase. Subsequent to Pearson et al. (2003), based on revised chemical modelling of waters sampled from dedicated boreholes, Pearson et al. (2011) determined that the generic selectivity coefficients are inappropriate for describing Na–K exchange in the Opalinus Clay at Mont Terri Tunnel. However, selectivity coefficients for different kinds of rocks can differ significantly (e.g. c.f. Pearson et al., 2011 and Gaucher et al., 2009). Hence it is not necessarily the case that the selectivity coefficients in Parkhurst and Appelo (1999) would be inappropriate for the KCF and the OCF even if they are inappropriate for the Opalinus Clay.

Given the early stage of NWS’ investigations of LSSRs and the lack of data, the approach of Pearson et al. (2003) was used for modelling cation exchange when calculating reference porewater compositions for the KCF and OCF. The selectivity coefficients used being those from Parkhurst and Appelo (1999):

- $X^- = X^-$; log K = 0
- $X^- + Na^+ = NaX$; log K = 0
- $X^- + K^+ = KX$; log K = 0.7
- $2X^- + Ca^{2+} = CaX_2$; log K = 0.8
- $2X^- + Mg^{2+} = MgX_2$; log K = 0.6

Here X represents the exchanger and K is the selectivity coefficient; unlike equilibrium constants for other chemical equilibria (e.g. among aqueous species) K is relative to a single exchange species.

Details on the selection of CEC values and equilibrium constants are also given in Section 2.

The LSSRs considered in this report are typically bounded by aquifers. At the margins of these LSSR formations therefore, the water composition will be like that found presently in the aquifers. The porewater lying at the centre of the formation on the other hand, is the most likely water to be close to original depositional water (either halite-saturated water in the case of the MMG, or diagenetically modified seawater in the cases of the OCF and KCF). Between the centre of a considered LSSR and its margins, the porewater will be a mixture between the waters lying at these locations; the proportion of bounding aquifer water will increase towards the margin of the LSSR. In this diffusively mixed region, the concentration of some ions will reflect conservative binary mixing between the two end members (e.g. Cl). Other ions will exhibit non-conservative behaviour as their concentrations are buffered by mineral-fluid reactions during diffusive mixing. Models of Type 4 were used to simulate this mixing in order to determine compositions for alternative reference waters, between those in the formation centres and those at the margins (Mazurek et al., 2009). The general approach to modelling is illustrated in Figure 6.

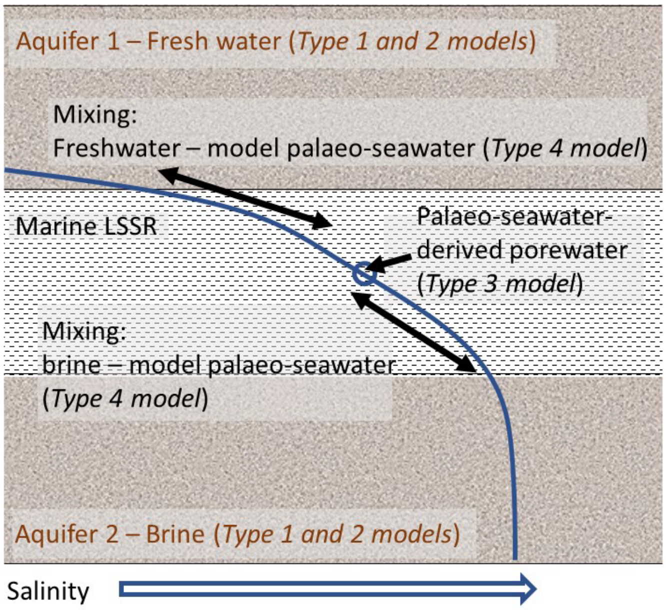

Figure 6. Schematic illustration showing general approach using the different kinds of model.

3.6 HOST ROCK TYPES OF INTEREST

3.6.1 Overview

Four host rock types of interest are considered in this study, the MMG, Massive Evaporite within the MMG, KCF and OCF. These rocks are present at depth in the regions where communities have engaged with NWS, via Working Groups and Community Partnerships.

Stratigraphic relations of the rock types of interest across England are shown in Figure 7.

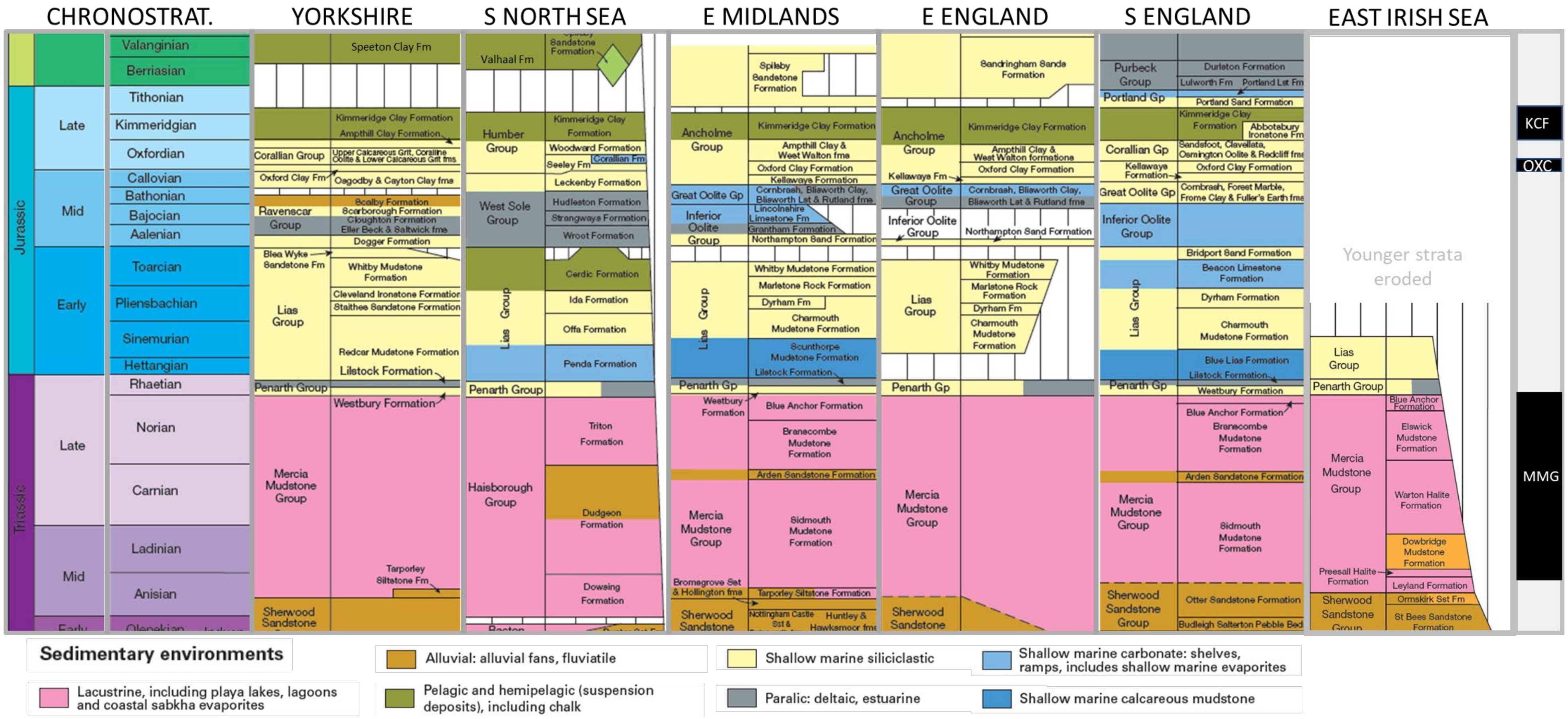

Figure 7. Stratigraphy of the rock types of interest across England. Formations of interest are abbreviated: MMG: Mercia Mudstone Group, OCF: OCF and KCF: Kimmeridge Clay Formation (after Waters et al., 2007a; Waters et al., 2007b). Contains British Geological Survey materials © UKRI (2007).

3.6.2 Kimmeridge Clay Formation (KCF)

3.6.2.1 SPATIAL DISTRIBUTION AND STRATIGRAPHICAL RELATIONS

The KCF is a Late Jurassic (Kimmeridgian) marine mudstone. In southern England, it occurs between siliciclastic limestones of the Corallian Group and Portland Group (Figure 8). The KCF is present in southern and eastern England, the two blocks separated by a break created by sub-Cretaceous erosion across the Anglo-Brabant Massif (Figure 8).

In the English Midlands and East Midlands Shelf, the Corallian Group is absent, and a thick sequence of Ancholme Group sediments is present. The KCF (and Ancholme Group) are overlain unconformably by Sandringham Sands and the Spilsby Sandstone Formation in eastern England. In North Yorkshire and the Southern North Sea, the KCF is overlain unconformably by the Speeton Clay Formation.

The KCF of southern England occupies a deep sub-circular depression centred on the Weald Basin (Figure 8). In eastern England, the formation dips north-eastwards from the East Midlands Shelf toward the Sole Pit Trough. The formation is absent from the Market Weighton Block.

The KCF reaches its maximum thickness of around 600 m in the Weald and Portland-Wight Basins (Appendix 2: Figure 23, Figure 24) but is eroded beneath the Early Cretaceous unconformity around the north-west margins of the Wessex-Weald Basins and South Dorset High. In eastern England, the formation is mostly less than 250 m thick (although it forms part of the much thicker mudstone unit defined by the Ancholme Group). The thickest onshore deposits occur south of the Humber and in the Cleveland Basin, but are attenuated onto the Market Weighton Block and the Anglo-Brabant Massif (Appendix 2: Figure 25).

Distributions of the KCF at 400–600 mOD are shown in Figure 9 and Figure 10. This depth range was selected for mapping as a central zone of the GDF depth range of interest of 200–1000 m. The range is selected in order to bound the study and provide location information of relevance for mid-point reference groundwater/porewater compositions.

3.6.2.2 ORIGIN AND MINERALOGY

Sedimentation of the KCF took place in a calm marine environment, with water depths of around 50–100 m. While conditions were largely stable for several million years, fluctuations in the amount of oxygen controlled irregular redox changes in cycles of sedimentation, with anoxia common (Oschmann, 1988).

Grey marine mudstone forms the dominant lithology (Gallois, 2004b). This is punctuated by well-cemented mudstones and carbonates (“stone-bands”). Organic-rich mudstones are most abundant in middle parts of the sequence. In southern England, the formation becomes sandier and siltier in the uppermost part beneath the Portland Group. In the deepest and thickest KCF of the Weald Basin, three thick micritic limestones form a conspicuous part of the stratigraphy (Appendix 2: Figure 25).

Mineralogy is dominated by clay minerals, with quartz, carbonates, organic matter and some sulphide minerals (Thomas and Holliday, 1982). Summary mineral data for three examples of the KCF are given in Table 12. These include an organic-rich group from the North Sea Basin. At Milton in Oxfordshire, the matrix of the KCF is dominated by detrital illite and kaolinite, with minor proportions of chlorite and mixed-layer illite-smectite. At Marcham in Oxfordshire, the KCF is dominated by detrital quartz and mica, with calcareous shell debris. The clay mineral matrix comprises kaolinite, illite and chlorite. In both these areas, pyrite is abundant and frequently concentrated along bedding laminae (Alexander et al., 1987).

Table 12. Mineralogy of the Kimmeridge Clay Formation (KCF) from published literature (% distributions).

Mineral	Fishman et al. (2012) North Sea Offshore n =19	(Alexander et al., 1987) Middle Thames, Oxfordshire
Quartz	24–37	23–34
K feldspar	4–9	present
Plagioclase	3–5	
Dolomite	0.3–4	
Pyrite	3–12	1–3
Amphibole	0.2–2	
Kaolinite	0–2	14–27
Smectite	0–3	
Illite	22–42	major
Mica	5–12	major
Chlorite	1–6	present
Organic carbon	4–9	
Calcite		2–5
Mixed-layer clay		present
Gypsum		present

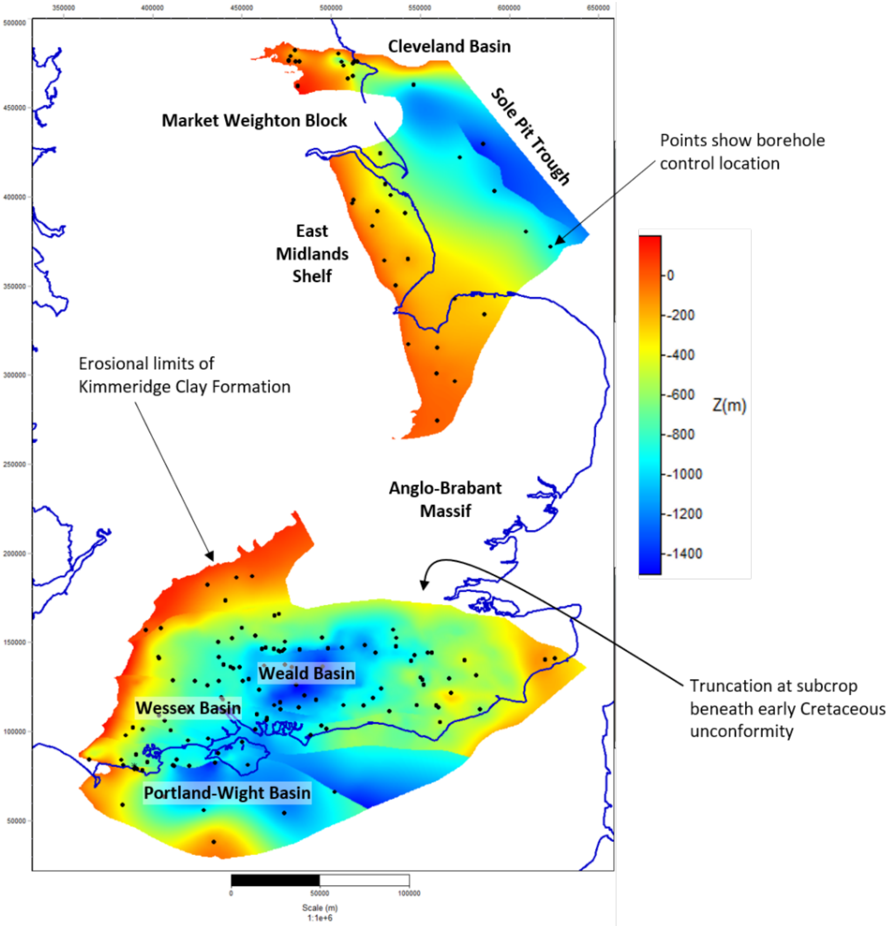

Figure 8. Elevation of the base of the Kimmeridge Clay Formation (KCF) across England and offshore (outcrop and subcrop). Geological structure and thickness maps throughout the report were generated for the purpose of this study. Surface is interpolated from borehole data (position of control boreholes is shown as black points). Areas beyond borehole control are subject to uncertainty.

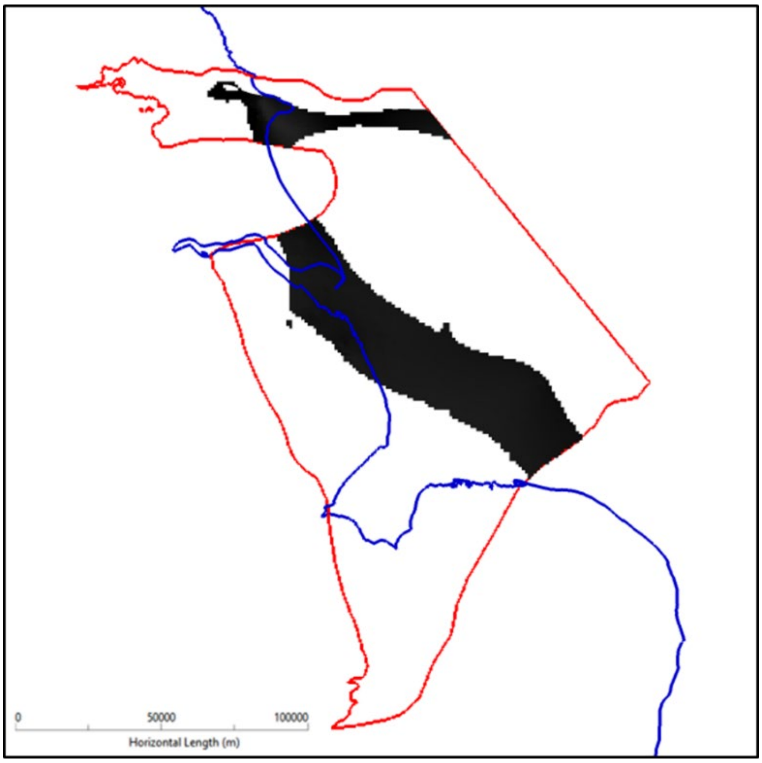

Figure 9. Occurrence of Kimmeridge Clay Formation (KCF) between 400–600 mOD in eastern England including offshore (total extent shown by red outline).

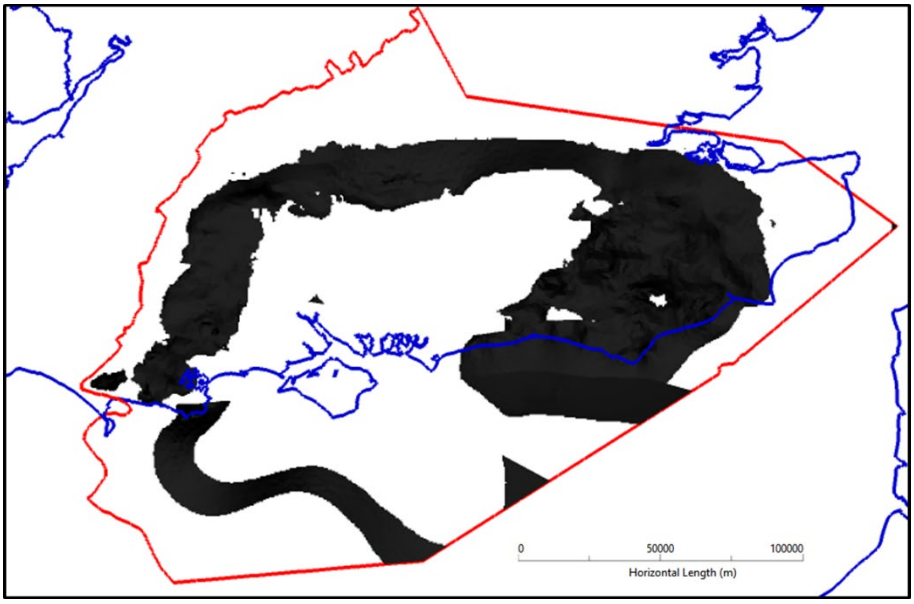

Figure 10. Occurrence of Kimmeridge Clay Formation (KCF) between 400–600 mOD in the Wessex Basin including offshore (total extent shown by red outline).

3.6.2.3 BURIAL HISTORY

Sedimentary deposition in two distinct basins in the Upper Jurassic was controlled by pre-Permian structures (Williams, 1986). In the south (e.g. Wessex Basin, Weald Basin), deposition was generally continuous into the early Palaeocene, while in northern and eastern England, basins underwent uplift and erosion at the end of the Jurassic, removing much of the KCF (Scotchman, 1991). In east Lincolnshire, uplift took place at the end of the Jurassic, with subsequent deposition up to the Early Cretaceous, and further burial in the Late Cretaceous. In the most northerly portion of the KCF, the Cleveland Basin, the burial history was similar to that in southern England, with continuous deposition and burial until the Late Cretaceous (Scotchman, 1991). Combined petrographic and fission track evidence has suggested that the Middle Jurassic strata of the Cleveland Basin were buried to depths of 2–3 km before inversion, uplift and compression during the late Cretaceous and early Palaeocene, associated with the Alpine Orogeny (Hemingway and Riddler, 1982; Powell, 2010). Inversion, uplift and erosion occurred across all basins (Scotchman, 1991). Organic matter in the KCF deposits ranges from immature to mature depending on history of burial depth (Fishman et al., 2012).

3.6.3 Oxford Clay Formation (OCF)

3.6.3.1 SPATIAL DISTRIBUTION AND STRATIGRAPHIC RELATIONS

The Mid-Late Jurassic OCF is a grey marine mudstone which in southern England occurs between the sandy clays and sandstones of the Kellaways Formation and the limestones of the Corallian Group (Figure 7). In Yorkshire, the Osgodby Formation replaces the Kellaways Formation at the base. In eastern England and the Midlands, Corallian Group limestones are replaced by mudstones of the West Walton Formation. The upper lithological boundary of the OCF is thus less distinct and forms part of a thick succession of Jurassic mudstones (the Ancholme Group) that includes the Kellaways, Oxford Clay, West Walton, Ampthill Clay and Kimmeridge Clay formations.

The OCF occurs in a broad tract between south Dorset and north Yorkshire (Figure 11). The eastern onshore boundary is a concealed erosional truncation around the flanks of the Anglo-Brabant Massif which lacks a cover of OCF. The western boundary is an erosional truncation at outcrop. OCF is absent from the Market Weighton Block.

The formation arches across the Anglo-Brabant Massif, dipping southwards into the pit-like depression formed by the Weald and Portland-Wight Basins and north-eastwards across the East Midlands Shelf. It continues offshore and flanks the Sole Pit Trough in the Southern North Sea (Figure 11).

The OCF has a well-defined thickness pattern, increasing from north-east to south-west (Appendix 2: Figure 27). The maximum thickness occurs in south Dorset where it reaches 220 m thick in the Portland-Wight Basin. The formation is typically less than 80 m on the East Midlands Shelf, thickening into the shallow sag-like depression between the Anglo-Brabant Massif in the south and the Market Weighton Block in the north (Figure 11).

Distributions of the OCF in the central portion of the depth range of interest for the GDF (-200 to -1000 m) are shown in Figure 12.

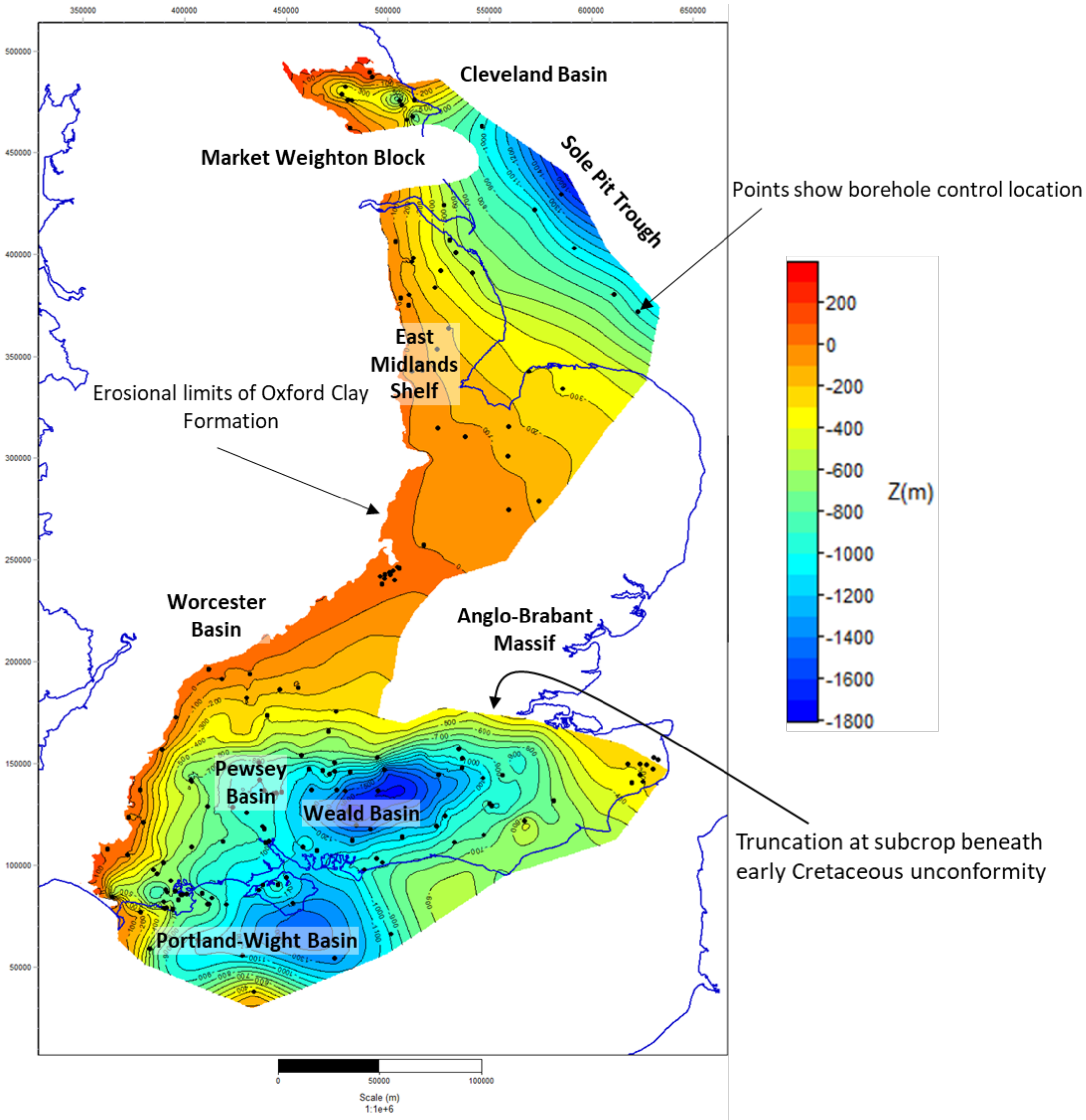

Figure 11. Elevation of the base of the Oxford Clay Formation (OCF), east and southern England.

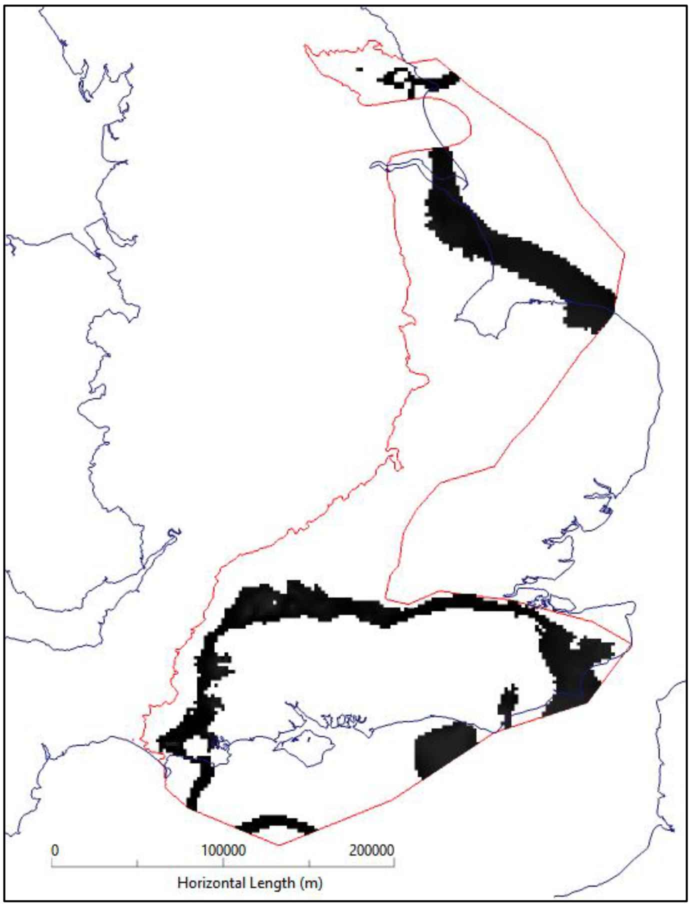

Figure 12. Occurrence of the Oxford Clay Formation (OCF) between 400 and 600 mOD, eastern and southern England and offshore (total extent shown by the red outline).

3.6.3.2 ORIGIN AND MINERALOGY

The OCF was deposited in an inland sea during a transgressive phase. Grey marine mudstones are the characteristic lithology of the OCF, but silty and sandy mudstones occur at the base in South Dorset and the sequence is punctuated throughout by cemented mudstones and muddy limestones. The limestones become particularly well-defined across the southern English Midlands in the central part of the formation. Their occurrence, thickness and lateral continuity are important to the regional flow of groundwater. Organic-rich mudstones are primarily concentrated toward the base of the formation. In eastern England, a deepening of the depositional basin is reflected by the organic-rich argillaceous facies of the Peterborough Member becoming generally more calcareous and less organic-rich upwards into the Stewartby Member (Belin and Kenig, 1994).

Mineralogy of the OCF is dominated by clay minerals, with carbonates, quartz, organic matter and sporadic pyrite (Thomas and Holliday, 1982). Summary mineral data for the OCF are given in Table 13. Clays are typically dominated by illite and kaolinite with subordinate smectite; an organic carbon content of 1–5 wt% has been reported for the OCF of the UK (NEA, 2000).

Table 13. Mineralogy of the Oxford Clay Formation (OCF) from published literature (% distributions).

Mineral	NEA (2000)	Peterborough Member Norry et al. (1994) n=3
Illite	14–33	28–32
Chlorite	<5	7–8
Kaolinite	14–33	9–10
Illite-smectite	trace	
Quartz	11–28	22–24
K feldspar	trace	1–2
Calcium carbonate	0–2	
Pyrite	0–3	1–2
Organic carbon	1–5	remainder
Water content	9–20 dry wt	
Calcite		8–13
Siderite		1–2
Plagioclase		5–6
Gypsum		1–2
Apatite		trace
Anatase		1

3.6.3.3 BURIAL HISTORY

Sea-level rise across Britain during the early Callovian stage of the Middle Jurassic led to widespread inundation and sedimentation which resulted in the marine muds of the OCF. The formation appears to have been deposited relatively continuously within a deep Jurassic sea (Jackson and Fookes, 1974). As these sediments were buried, it is likely they compacted by up to 80% (Hart et al., 2019).

Deposition of the OCF was succeeded by the Corallian Group carbonate deposits during a period of marine shallowing, followed by a further sea-level rise which returned fully marine deeper-water conditions and to the deposition of the KCF, as described in Section 3.6.2.3.

Inferred former depths of burial of the OCF, from compilations of stratigraphical columns, vary from 300 m in Lincolnshire (Jackson and Fookes, 1974), to 500 m in Peterborough (Hudson and Martill, 1994) and Stewartby, Bedfordshire (Hudson, 1978) and up to 1500 m in Dorset (Jackson and Fookes, 1974). The shallow burial of OCF in the East Midlands was inferred from immaturity of organic matter and the excellent preservation of aragonite (Hudson and Martill, 1994).

3.6.4 Mercia Mudstone Group (MMG)

3.6.4.1 SPATIAL DISTRIBUTION AND STRATIGRAPHICAL RELATIONSHIPS

The mid to late Triassic MMG overlies the Sherwood Sandstone Group and passes upwards into the Penarth Group and Lower Jurassic marine mudstones (Figure 7). In north-west England and offshore, the MMG occurs in a series of isolated fault-bounded basins that include the Staffordshire Basin, Cheshire Basin, EISB and Solway Firth Basin.

In the EISB, the Jurassic is mostly truncated (Figure 7) and the MMG formation lies beneath a cover of Quaternary deposits which form the sea-floor (Scorgie et al., 2021). The deepest part of the EISB has an exceptionally thick sequence (4375 m) of Triassic strata (Jackson and Mulholland, 1993). Faulting means that the Triassic sequence is much thinner further east in the West Lancashire Basin, with MMG represented only by some 50 m of Tarporley Siltstone Formation below 40 m of Quaternary sediments at Formby (Scorgie et al., 2021).

In southern, central and eastern England, the MMG occurs in a broad tract between south-west Dorset and north-east Yorkshire (Figure 13), the eastern boundary of which is defined by an onlap pinch-out against the Anglo-Brabant Massif. The MMG does not extend across the Weald Basin.

The MMG occurs at shallow elevations across central England and the onshore parts of the East Midlands Shelf (Figure 13). In its main tract, the MMG thickens away from the Anglo-Brabant Massif in a broadly radial pattern. In southern England, it thickens progressively to the south-west, reaching around 600 m thick in the Portland-Wight and Lyme Bay Basins (Appendix 2: Figure 33). In north-east England, it thickens northwards and eastwards toward the Sole Pit Trough, where it reaches 500 m thick.

Distributions of the MMG in the central portion of the depth range of interest for the GDF (-200 to -1000 m) are shown in Figure 14 and Figure 15.

3.6.4.2 ORIGIN AND MINERALOGY

The MMG is dominantly a red (occasionally green-grey) siliciclastic mudstone with calcareous and silty mudstones, occasional sandstone and some beds of halite. Anhydrite and gypsum are present in some horizons; cements are typically carbonate and occasionally gypsum.

Deposits of MMG accumulated due to subsidence in fault-bounded inland basins created by crustal tension. Thick deposits were produced over much of central and southern England, the East Irish Sea Basin and North Sea Basin (Cowan et al., 1999; Howard et al., 2008), with thickness reaching up to 1350 m in the Cheshire Basin (Howard et al., 2008). Strata were deposited in a continental, largely mudflat, setting under hot, arid conditions. Silts and fine sands in the MMG derived from intervals of flash flooding. Layered halites in the sequence are interpreted as the products of shallow lakes or ponds concentrated by evaporation following episodic marine flooding (Arthurton, 1980). Diagenesis produced subsequent carbonate and gypsum cements. The depositional setting contrasts strongly with the facies of the KCF and OCF.

The MMG is divided (in sequence upwards) into the Tarporley Siltstone Formation, Sidmouth Mudstone Formation, Arden Sandstone Formation, Branscombe Mudstone Formation and Blue Anchor Formation.

Reddish brown mudstone forms the characteristic lithology of the MMG at outcrop. However, basin marginal conglomerates and breccias, sandstones, dolomitic siltstones, gypsum, anhydrite and halite also occur (Armitage et al., 2016). In the clay-dominant sections, illite is typically the most abundant clay mineral, but with subordinate chlorite. Illite and chlorite are detrital, with mixed-layer clays being an authigenic component (illite-smectite or chlorite-smectite) (Hobbs et al., 2002; Milodowski et al., 1994). Detrital mica is also present (Arthurton, 1980). Quartz dominates the non-clay fraction; calcite and minor feldspar are also present. Horizons also contain occasional anhydrite/gypsum, dolomite and halite. Mid-grey mudstones contain occasional pyrite (Arthurton, 1980). Iron(III) oxide in coatings and cements, giving a typically red-brown colour, is indicative of deposition in oxic conditions characteristic of wind-blown detrital material in a hot, arid environment (Hobbs et al., 2002). Grey-green horizons are associated with presence of organic matter, giving locally Fe-reducing conditions, with occasional pyrite. Ferroan dolomite and ankerite have been found as diagenetic overgrowths of earlier dolomite (Hobbs et al., 2002). Formation of authigenic smectite, along with dolomite and gypsum have been linked with saline diagenetic water rich in Mg (Bloodworth and Prior, 1993). Magnesium-rich authigenic palygorskite and sepiolite may also be present as accessories (Milroy et al., 2019). Anhydrite/gypsum and halite are rarely found in the near-surface due to dissolution (Hobbs et al., 2002).

Table 14. Mineralogy of the Mercia Mudstone Group (MMG) from the published literature (% distributions).

Mineral	M5 motorway Worcestershire (n=7)	Blaby, Leicestershire (n=3)	M50 motorway Worcestershire and Gloucestershire (n=3)	Willow Farm borehole, near Nottingham, 300–310 m deep (n=6)
Source	Dumbleton (1967)	Dumbleton (1967)	Dumbleton (1967)	Armitage et al. (2016)
Illite	28–56	29–33	40–54	4–40
Chlorite	11–35	8–18	17–39	2–6
Quartz	6–24	30–35	7–15	32–66
Calcite	4–24	7–11	4–11	0–3
Dolomite	1–3	4–9	3–5	1–12
Hematite	1–2	1–2	1–2	
Sepiolite	11–41		trace	
Palygorskite		5–8	<10	
K-feldspar				6–16
Plagioclase				0–2
Gypsum				0–19

3.6.4.3 BURIAL HISTORY

In the Mersey/Cheshire Basin of north-west England, deposition of the continental MMG was followed by deposition of some 450 m of Jurassic marine sediments. Tellam (1995) inferred some dewatering of deposits of the lower MMG during the Jurassic. Non-deposition and erosion during the Cretaceous, probably accompanied by freshwater influx (Metcalfe et al., 2000) was followed by uplift and inversion during the Palaeocene (inversion possibly of Miocene age: Naylor et al. (1989)). Subsequent erosion, with freshwater and then marine inundation is inferred for the Palaeocene and with further periods of both high and low sea level during the Quaternary. This complex history of inundation and flushing would likely have led to a modern shallow freshwater system above saline water at depth. Tellam (1995) inferred a maximum burial depth of 950 m for the base of the MMG in the Cheshire/Merseyside area. Scorgie et al. (2021) suggested for core material from a borehole at Formby, Merseyside, that MMG sediments had been buried to depths at least 1000 m but probably not as deep as 2000 m. Depth of burial was likely greater for the MMG in the EISB. Colter (1978) inferred from geophysical and vitrinite reflectance data that the MMG had likely been buried formerly to depths around 2000 m. Jackson and Mulholland (1993) also tentatively inferred 2000–2500 m of erosion and uplift post the early Jurassic EISB.

Around Cumbria, late Cimmerian tectonics and uplift during the early Palaeocene produced the Lake District massif and caused large changes to hydraulic gradients and likely consequences for increased groundwater movement. Some 2000 m of Mesozoic sedimentary rocks are thought to have been eroded from the EISB during the Palaeocene (Bath et al., 2006). Oxygen and deuterium stable-isotopic compositions of groundwater in the Sherwood Sandstone Group of west Cumbria (Sellafield) suggest intervals of flushing of the aquifer during the Quaternary, with recharge of groundwater mainly of Holocene age (Bath et al., 2006). Further, the stable-isotopic compositions were inconsistent with a seawater origin for the saline groundwaters.

The MMG of the English East Midlands is also inferred to have been buried to maximum depths of some 2000–2500 m and to have reached temperatures up to 80°C (Armitage et al., 2016).

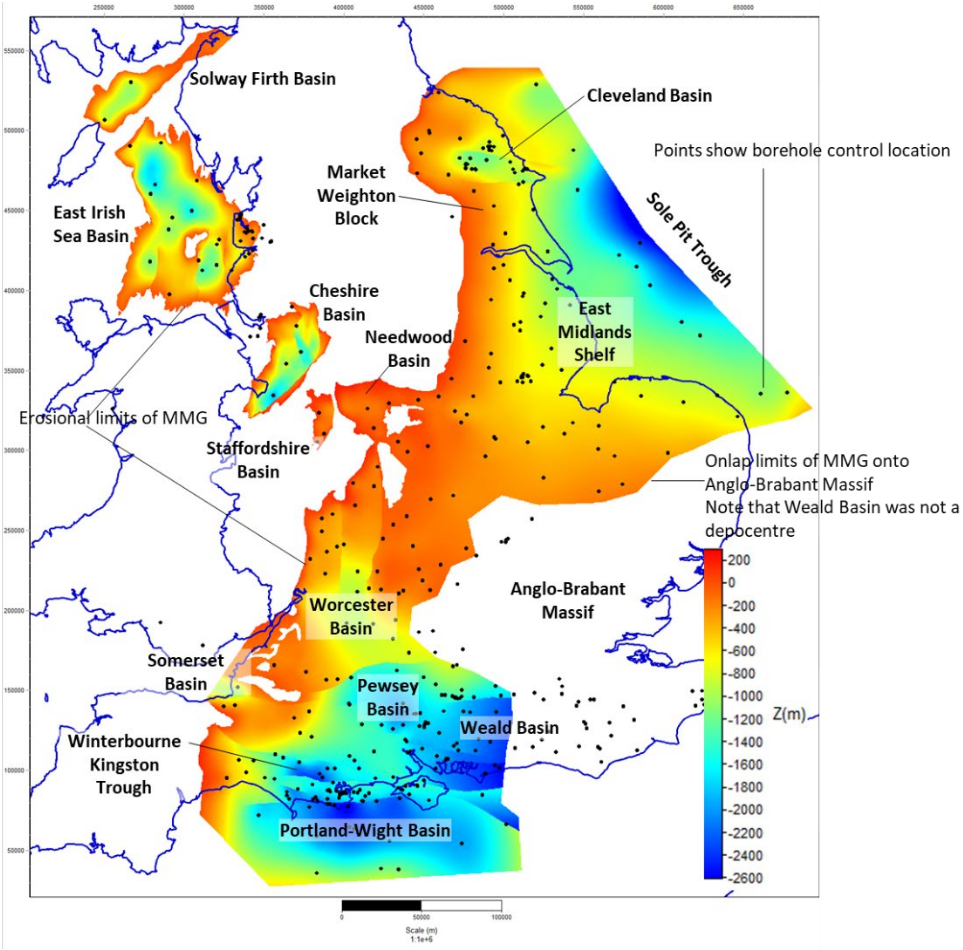

Figure 13. Elevation of the base of the Mercia Mudstone Group (MMG) with major basins and highs across England and offshore (outcrop and subcrop).

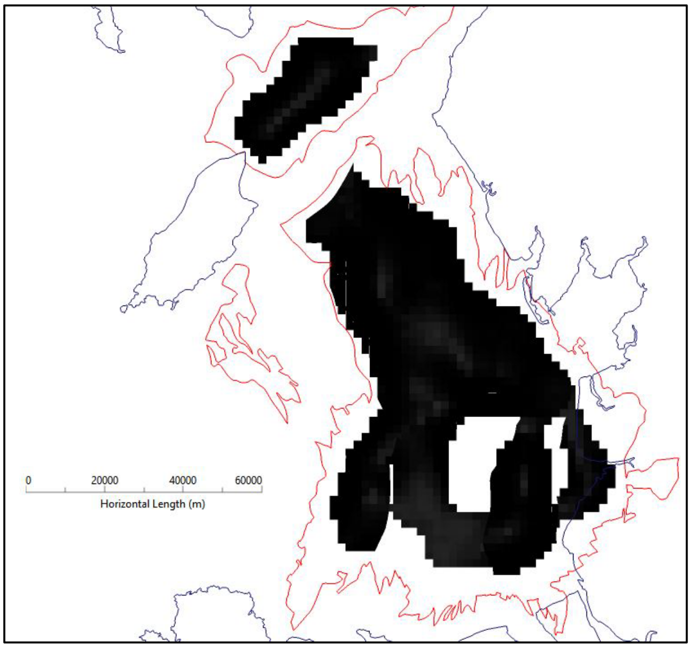

Figure 14. Occurrence of the Mercia Mudstone Group (MMG) between 400 and 600 mOD, East Irish Sea Basin (total extent shown by red outline).

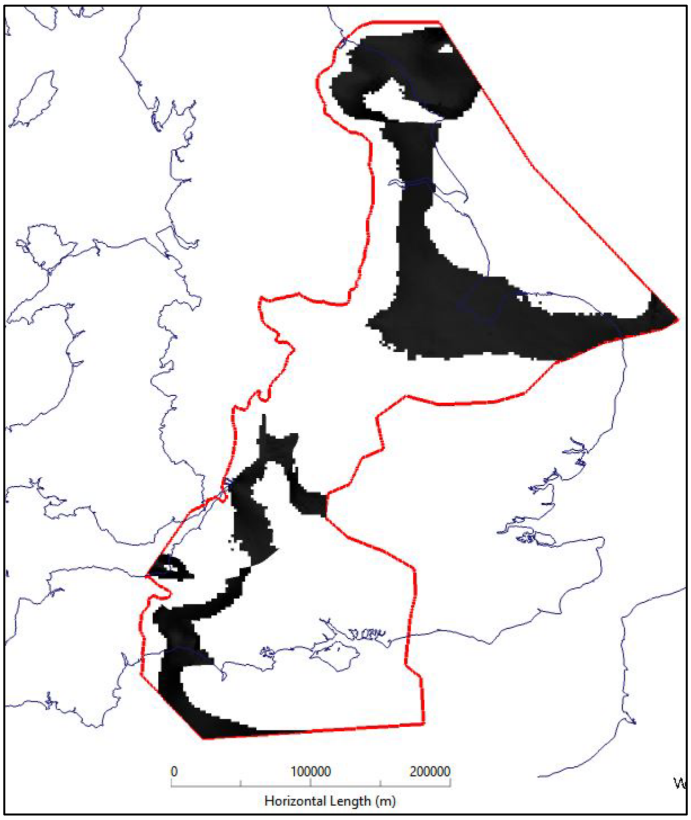

Figure 15. Occurrence of the Mercia Mudstone Group (MMG) between 400 and 600 mOD in east and southern England including offshore (total extent shown by red outline).

3.6.5 Mercia Mudstone Group (MMG) evaporites

3.6.5.1 REGIONAL OCCURRENCE

The main onshore halite deposits within the MMG are located in south Dorset. These occupy a central part of the stratigraphy which ranges up to 500 m thick (Appendix 2: Figure 36). The halites are bounded below and above by thick reddish-brown mudstones and they also interbed with mudstones on multiple scales. Evaporites occur in the Dunscombe Mudstone Formation, with up to 30 m of halite in the Central Somerset Basin and up to 130 m in the Wessex Basin (Gallois, 2004a). These occur at generally more than 700 m depth. Halites also occur in the Cheshire Basin, Needwood Basin and in the northern part of the Worcester Graben.

Offshore, major halite deposits occur within the MMG of the East Irish Sea Basin, although these also extend onshore. Offshore, the halites interbed with reddish-brown mudstones at all scales (Appendix 2: Figure 37). The thickest halite with the lowest proportion of mudstone (Preesall Halite Formation) occurs toward the top of the MMG. On the shallow flanks of the basin, this unit may not be present due to a combination of thinning and erosional truncation. The Mythop, Rossall and Fylde halites have thick interbedded mudstones. In the East Irish Sea Basin, the Fylde Halite Member is restricted to the north and central parts (Cowan et al., 1999). The Fylde Halite Member forms a basal halite in the MMG sequence (Smith et al., 2005).

The Dorset halites are considered contemporaneous with the Droitwich Halite Formation of the Midlands, Wilkesley Halite Formation of the Cheshire Basin and the Warton Halite Formation of the Irish Sea Basin (Gallois, 2004a).

Across the onshore parts of the East Midlands Shelf, evaporites in the MMG are limited to thin anhydrites and nodular gypsum deposits.

3.6.5.2 ORIGIN AND MINERALOGY

As outlined in Section 3.6.4.2, the halite deposits layered within the MMG are considered the products of evaporation of shallow lakes or ponds which followed episodes of marine flooding (Arthurton, 1980).

Halite occurrence is extensive. In Cheshire it occurs in two major formations (the Northwich and Wilkesley Halites), which are mineralogically very similar, generally comprising 25% mudstone, 75% halite. The mudstones and siltstones which are interbedded with the halite contain gypsum/anhydrite and microcrystalline dolomite. One of the purest parts of the formation consists of 95% sodium chloride, with possible inclusions or laminae of gypsum/anhydrite and microcrystalline dolomite (Hobbs et al., 2002; Wilson, 1993). Such pure seams contain <2% insoluble material. The less-pure beds are mixtures of mudstones and displacive halite, known as “haselgebirge” (Gallois, 2004a).

Illite and chlorite occur within the mudstone and siltstone of the Northwich Halite Formation. Corrensite content of the clay mineral assemblage increases from absent at the base of the formation to an important component at the top. The clay-mineral assemblage of the Wilkesley Halite Formation contains fairly constant amounts of illite and corrensite, with minor amounts of chlorite (Hobbs et al., 2002).

3.6.5.3 BURIAL HISTORY

The MMG evaporites form part of the MMG; burial history is described for these units in Section 3.6.4.3.

3.7 ROCK PHYSICAL PROPERTIES

A brief overview of the physical properties of the rock types of interest collated from various literature sources is given in Table 15. These are included to provide further characterisation of the rocks but were not required in this report for the equilibrium modelling of water-rock interactions in the derivation of reference groundwater compositions. More detailed information on the petrophysical properties of mudrocks is available elsewhere (e.g. Aplin and Macquaker, 2011) and is beyond the present scope.

It should be noted that there are few reported measurements of physical properties for the considered rock formations over depth ranges relevant to a GDF in the areas covered by this report. Furthermore, those data that are available have been obtained using differing techniques on different materials and therefore are not directly comparable. For example, in Table 15 the intrinsic permeability range for the OCF is derived from field measurements in faulted sections of this formation (Hallam et al., 1991). This may explain why the minimum permeability identified for the OCF is substantially lower than that identified for the KCF.

Mudrocks are typified by low overall hydraulic conductivity such that solute transport by diffusion is an important factor. Intrinsic permeability is low but dependent on factors including the mineralogy of the LSSRs/evaporites, especially the content and types of clay minerals. For example, permeability of the OCF is found to be inversely related to illite content (Armitage et al., 2016). Total porosity is the ratio of voids to total rock volume, as distinct from advective (effective) porosity, which is that component able to contribute to fluid movement, and geochemical porosity, which describes the porosity accessible to mobile anions (e.g. Cl) and takes account of anionic repulsion in clays due to the negative surface charge (Gaucher et al., 2006). Total porosity varies but may be moderately high in some LSSRs (Table 15). The LSSRs described here have relatively high compressibility and so variations in hydraulic properties are likely with increasing depth (Tellam and Lloyd, 1981).

Table 15. Physical properties of the LSSRs and evaporites of interest (data sources: Armitage et al., 2016; Hallam et al., 1991; Hobbs et al., 2002; Horseman et al., 1996; Metcalfe et al., 2000; Metcalfe et al., 2015; Milodowski and Rushton, 2009; Raji, 2017; Tellam and Lloyd, 1981).

Rock type	Bulk density (kg/m^3)	Intrinsic permeability (m^2)	Total porosity
Kimmeridge Clay (KCF)	2010-2110	10^{-18}-10^{-20}	0.04–0.07
Oxford Clay (OCF)	1710-2100	10^{-15}-10^{-19}	0.03–0.05
Mercia Mudstone (MMG)	1870–2420	10^{-17}–10^{-20}	0.20–0.40
Evaporite	2030–2090	10^{-16}–10^{-23}	0–0.04

Diffusivity data are lacking for the considered rock formations over the relevant depth ranges. Based on their broadly similar porosities and lithological characteristics, the KCF and OCF are likely to have effective diffusion coefficients (D_e) that are of similar orders of magnitude. The MMG is a more lithologically variable formation than either the KCF or the OCF and therefore D_e values of the MMG rocks are likely to be more variable than those of the KCF or OCF. The more clay-rich, finer-grained lithologies within the MMG could have similar D_e values to those of the other two formations. However, much of the MMG is poor in phyllosilicates and has higher porosities than the KCF or the OCF. Hence, the MMG is likely to mostly have higher D_e values. Halite-dominated evaporite formations will have very little connected porosity and probably would have lower D_e than the considered siliciclastic formations. However, evaporite formations that are dominated by evaporite minerals less deformable than halite, such as anhydrite- or gypsum-dominated formations, are expected to have higher D_e than halite-dominated formations.

Reported D_e obtained from argillaceous rocks that have been investigated in connection with radioactive waste disposal in other countries give some pointers towards credible D_e values for the KCF and OCF. However, there are no good international analogues for the MMG.

Data from other countries show that effective diffusion coefficients depend on the characteristics of the solute (to a large extent whether anionic, cationic or neutral), the temperature, and the rock properties including anisotropy. Van Loon (2014) reported that in the Opalinus Clay in Switzerland ${}^{Na}D_e$ > ${}^{HTO}D_e$ > ${}^{Cl}D_e$, and that at 70°C, D_e values for a given solute are typically around 25% to 30% greater than at 25°C. Van Loon (2014) also reported that perpendicular to bedding, D_e ranges from 1.7×10^{-13} to 5.6×10^{-10} m^2/s. Based on transport modelling to match ^{4}He data obtained from the Opalinus Clay in Mont Terri Tunnel, Pearson et al. (2003) determined apparent diffusion coefficients of 2×10^{-11} m^2/s to 4×10^{-11} m^2/s.

Mazurek et al. (2009) reported diffusion coefficients for a range of argillaceous rocks in addition to the Opalinus Clay. In the Callovo-Oxfordian shale at Bure, D_e for HTO, Cl^- and cations were reported as 2.6×10^{-11} m^2/s, 5×10^{-12} m^2/s and 2.5×10^{-10} m^2/s respectively (all at 20°C). The authors reported D_e for the Boom Clay in Belgium of between 8.5×10^{-11} m^2/s and 4.6×10^{-10} m^2/s for isotopes of H and O in water and between 2.2×10^{-11} m^2/s and 4×10^{-10} m^2/s for anions.

Based on the distance for which natural CO_2 has diffused from a reservoir formation into a caprock composed of KCF in the Brae field of the North Sea, Skurtveit et al. (2019) proposed an effective diffusion coefficient of 10^{-14} m^2/s. This value is much lower than reported for argillaceous rocks in the other countries described above. However, the bottom of the KCF in the Brae field is at almost 4000 m depth, very much deeper than a GDF. It is to be expected that pore connectivity will be less and hence diffusion lower under the stresses at these greater depths. Additionally, dissolution of CO_2 in porewater and subsequent reaction of the acidified water produced with minerals in the rock will effectively slow migration of CO_2, thereby resulting in a smaller effective diffusion coefficient (e.g. Kampman et al., 2016). It is therefore reasonable to suppose that the considered LSSR would have intrinsic D_e at GDF depths higher than 10^{-14} m^2/s for most conservative ions. However, it is important to consider that the diffusion of reactive solutes (for example many radionuclides) will be similarly retarded by mineral, surface complexation and ion-exchange reactions.

Based on measured free water diffusion coefficients for a range of aqueous solutes and porosities and estimated tortuosities, a reasonable D_e value for halite is in the order of 10^{-13} m^2/s and a reasonable D_e value for anhydrite is an order of magnitude greater at 10^{-12} m^2/s (Sevougian et al., 2015).

3.8 DATA COMPILATION AND QUALITY ASSESSMENT

3.8.1 Data availability

A map of the locations of samples of groundwater/porewater collated for this study is shown in Figure 16. Distribution of the onshore outcrops of the LSSRs of interest is also shown for reference. The map demonstrates the paucity of publicly available water data for England and the resultant challenges involved in deriving reference water chemical compositions at the depth ranges of interest.

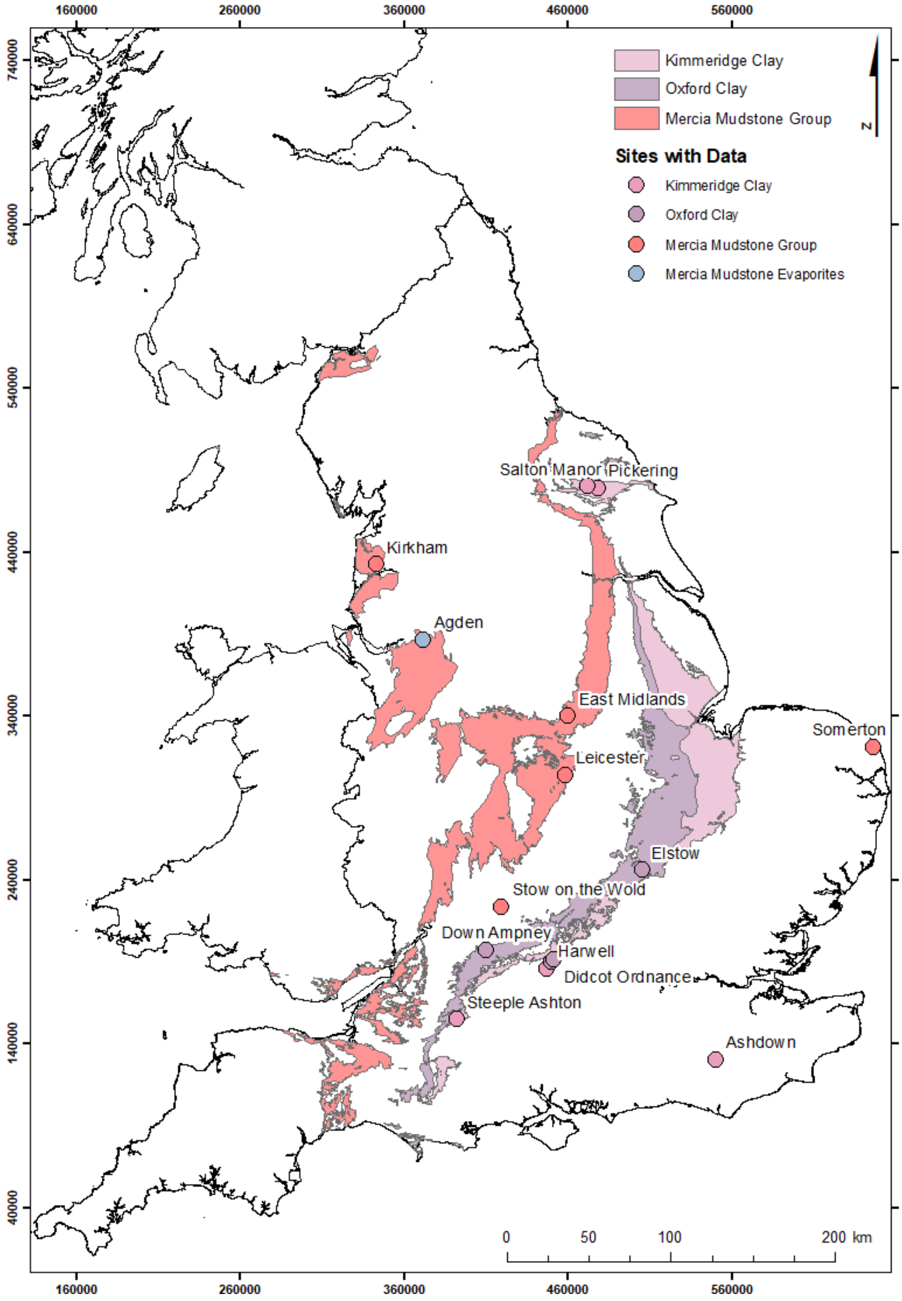

Figure 16. Locations of groundwater/porewater samples from LSSRs identified in this study, with distributions of rock formation outcrops. Contains BGS data © UKRI 2022 and OS data © Crown copyright and database right 2022.

3.8.2 East Irish Sea Basin

3.8.2.1 GROUNDWATER/POREWATER COMPOSITIONS

Searches of the data sources outlined in Section 3 found no compositional data for porewater/groundwater from the MMG offshore at depths >200 m in the East Irish Sea Basin. The nearest proxy data were identified from an observation borehole in Kirkham, Lancashire (Figure 16 given before), from which bailed depth samples[4] have been collected in the depth range 240–350 m, by both the Environment Agency and BGS (Table 16, average of 4 analyses). The borehole log identifies units of Breckells, Kirkham, Singleton and Hambleton Mudstones within the MMG and indicates that the lithology is dominated by red-brown

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[4] Borehole depth and dimensions mean that purging three borehole volumes would require removal and disposal of some 35 cubic metres of hypersaline groundwater

mudstone with abundant siltstone, and with common gypsum crystals and/or veins. Halite pseudomorphs are also recorded, notably at 320–330m and 350–358m depth; calcite veining is also found in parts.

The data summarised in Table 16 include analyses summarised by Ove Arup and partners Ltd, commissioned by Cuadrilla Bowland Limited, in preparation of an Environmental Statement for exploratory deep drilling and testing in the Fylde, Lancashire (Arup, 2014). The Arup report presented two analyses from the Kirkham borehole provided by the Environment Agency. The report states the total borehole depth as 445 m with a completion in the Sherwood Sandstone Group, in accordance with the geological log. The borehole is plain-cased to 134 m below ground level and open-hole below. Two groundwater samples were collected unpurged with a bailer at 240 m and 260 m depth (Arup, 2014). Limitations of data quality apply for unstable parameters (temperature, DO and possibly pH); redox-sensitive solutes in these samples (possibly Fe, Mn) may also be of lower reliability.

A bailed depth sample was also collected by BGS in 2015, also without purging. The sampling was part of early environmental baseline monitoring investigations (Ward et al., 2018). The sample was collected with a mechanised addressable sampler. Geophysical logging during the BGS investigation revealed that the borehole had collapsed at 354 m depth, above the base of the MMG strata which the lithological log demonstrated at 367 m depth. The sample was taken at 350 m.

Samples collected by BGS for dissolved-gas analysis were collected using a small suction pump at the surface to transfer the water from the addressable sampler into a pressure vessel. Temperature, pH, Eh and DO were not measured given the sampling challenges. The dissolved gases and redox-sensitive analytes (Fe, Mn) may have been affected to some degree by the sampling methodology, although acid preservation minimised the impact on metal concentrations.

The most recent analysis from the Kirkham borehole was produced by the Environment Agency and reported by Wilson et al. (2019). All data used in that study were downloaded from the Environment Agency's Water Quality Archive, for the years 2000–2016.

All bailed samples were taken from open-hole sections of the Kirkham borehole and are taken to originate from relatively permeable horizons in the MMG. The groundwater is hypersaline with TDS estimated at 170,000 mg/L (roughly five times seawater salinity; Cl average concentration 77,000 mg/L); Na and Cl are the dominant ions. These features are seen in all four analyses and give reasonable confidence in the chemistry of the water samples presented in Table 16, with the possible exception of pH. Nonetheless, the observed pH range was relatively small (7.2–7.5). Groundwater is mildly reducing (NH_4 0.98 mg/L and with high concentrations of dissolved Fe, average 12 mg/L; measured concentrations of dissolved CH_4 were low, a single analysis yielding 0.007 mg/L and two <0.0005 mg/L). Data for groundwater temperature and DO are not presented in Table 16 due to low confidence in the results.

Table 16. Mean values for groundwater from the Mercia Mudstone Group (MMG) of Lancashire, DOC: dissolved organic carbon; concentrations in mg/L.

Location	Kirkham, Lancs
Type	GW
Depth (m)	240–350
no. samples	4
TDS	170,000
Ca	1260
Mg	473
Na	52,000
K	64
Cl	77,000
SO_4	6085
HCO_3	3
pH	7.4
Si	0.56
B	1.4
Li	2
Sr	18.5
NH_4	0.98
Fe	12.0
DOC	1.08
Source	EA WQA, BGS archives

GW: groundwater.

The groundwater salinity owes much to interaction of water with MMG sediments which have been subjected to evaporation and cycling of evaporite deposits (gypsum/anhydrite, halite) following initial deposition in a continental mud-flat environment.

Groundwater data for strata including evaporites in the MMG are equally sparse, with no information found for 400–600 m depth. Tellam (1995) provided data for three groundwater depth samples from a borehole identified to be from MMG including evaporites in the Mersey Basin (e.g. adjacent to the Northwich Halite Formation) in the depth range 70–150 m (Table 17). These were also sampled by bailing. Compositions show a large range of salinity but with a strong Na-Cl dominance and with a high concentration of SO_4 in the deepest most saline sample. High salinity, high SO_4, constant Br/Cl ratios and low overall K were inferred by Tellam (1995) to indicate an evaporite dissolution (halite, gypsum) origin. Modelling of the deepest water sample (150 m) suggested the composition was close to saturation with respect to halite and gypsum/anhydrite (as well as calcite) (Tellam, 1995). The Merseyside groundwaters studied were suggested to have been influenced to some extent by ion exchange as burial depths had likely been insufficient for reactions beyond smectite-to-illite transformation and so retained some ion-exchange capacity, unlike studies elsewhere in England.

The groundwater of the Mersey Basin appears to have been insufficiently reducing to effect SO_4 reduction and low NH_4 concentrations (if reliable) suggest little anaerobic degradation of organic matter. Relatively high concentrations of dissolved Fe suggest Fe-reducing conditions, probably around 0 mV ±200 mV (Tellam, 1995).

Table 17. Groundwater data from three depths in a borehole at Agden, Mercia Mudstone Group (MMG), Mersey Basin, strata include evaporite deposits, concentrations in mg/L.

Location	Agden Brine	Agden Brine	Agden Brine
Type	GW	GW	GW
Depth (m)	70	120	150
pH	7.0#	6.8#	5.75#
Temperature (°C)	22#	22#	22#
TDS	9050*	16,000*	321,000*
Ca	159	177	1224
Mg	12	22	411
Na	3350	5950	122,500
K	10	13	105
Cl	5000	9260	192,100
SO_4	434	481	4,690
HCO_3	41	35	135
Br	4	12	112
F	0.26	0.31	0.33
NH_4	<0.06	<0.06	<0.06
NO_3	3.84	2.13	0.04
Si	0.46	0.28	0.70
B	0.3	0.45	2.50
Fe	29	12	25
I		12	
Sr	4.9	3.6	30
TOC			
Source	Tellam (1995)	Tellam (1995)	Tellam (1995)

GW: groundwater; #Laboratory estimate; *by summation.

3.8.2.2 GROUNDWATER CHEMISTRY OF BOUNDING AQUIFERS

Sherwood Sandstone Group

The Sherwood Sandstone in the Cheshire/Mersey Basin onshore has fresh shallow groundwater, but increasing salinity at depth. In the Mersey Estuary area, saline groundwater originates from modern saline intrusion due to a history of overpumping. Elsewhere in the Cheshire Basin, deep saline groundwater of natural origin is identified at depths greater than around 200 m (Tellam, 1995). Groundwater chemistry including salinity varies, depending on whether the aquifer is confined below MMG and/or Quaternary till. In the marginal areas of the basin, absence of confining cover results in active groundwater recharge. In the central part, freshwater recharge is much more restricted due to cover by MMG as well as the poorly-permeable till. Groundwater in the deepest part of the confined aquifer of the Cheshire Basin is Na-Cl type (Cl >100,000 mg/L at >500 m depth) and the salinity most likely originates from halite dissolution (Metcalfe et al., 2000). The origin of the hypersaline brine at depth is not established but interaction between halite and groundwater within the lower part of the MMG followed by density-driven flow and mixing with fresher resident groundwater in the underlying sandstone has been inferred as the most likely mechanism (Metcalfe et al., 2000).

Data for groundwater compositions in the Sherwood Sandstone Group are given in Table 18. Hollins Lane, Merseyside and Fylde, Lancashire are two locations from Sherwood Sandstone confined below the MMG at more than 300 m depth; Stanlow, Merseyside is shallower (150 m) and not confined below the MMG. This is consistent with the groundwater at this last site being fresher and less reducing. The measured Eh at the site shows a sub-oxic composition (298 mV; Table 18), which is credible. Highest salinity is observed in the deep confined samples; waters in these are dominated by Na-Cl.

Table 18. Groundwater chemistry for selected deep boreholes in the Sherwood Sandstone Group, north-west England, concentrations in mg/L.

Location	Hollins Lane, Merseyside	Fylde, Lancs	Stanlow	Sellafield No 2	Sellafield No 3	Sellafield No 3	Sellafield No 3
Type	PW	GW	PW	GW-DET	GW-DET	GW-DET	GW-DET
Depth (m)	377	360	150	206	689	772	1106
TDS	108,000#	33,900#	4300#	165	113,000	117,000	188,000
Ca	1602	250	595	33	2320	2270	2520
Mg	424	127	89	11	494	465	686
Na	39,400	12,000	858	13	41,900	44,500	71,600
K	14	20	24	2	241	302	327
Cl	64,000	18,800	2410	12	64,200	65,800	108,000
SO_4	2607	2660	141	9	3580	3640	4910
Alk HCO_3	24	70	218	124	33	16	55
pH	7.5*	8.3	7.3				
Eh (mV)			298				
Br				0.1	65.4	69.1	96.6
Sr					51.4	51	54.3
TOC							
Source	Tellam (1995)	BGS archives	Metcalfe et al. (2000)	Bath et al. (2006)	Bath et al. (2006)	Bath et al. (2006)	Bath et al. (2006)

PW: porewater, GW: groundwater; DET: discrete extraction test; *laboratory measurement; #by summation.

Tellam (1995) listed data for Sherwood Sandstone Group groundwaters/porewaters. The deepest located in the study was porewater from a coal exploration borehole with a Cl concentration of 64,000 mg/L (Hollins Lane; Table 18). Tellam (1995) concluded that salinity of the Sherwood Sandstone groundwater from the Mersey Basin was due to evaporite dissolution.

A bailed groundwater sample from a borehole in the Fylde, Lancashire taken from the topmost part of the Sherwood Sandstone (just below MMG) had a Cl concentration of 18,800 mg/L (Table 18). The salinity of the groundwater in the deep confined Sherwood Sandstone implies an old groundwater having undergone a significant amount of water-rock interaction, with dissolution of evaporites being the dominant mineral source.

From Sellafield borehole No 3, groundwater from three depth intervals of the Sherwood Sandstone was sampled using Discrete Extraction Tests (DETs) involving isolation of 10–20 m sections of borehole using packers and gas lifting to surface using nitrogen (Bath et al., 2006). Chemistry of water from the three depths is given in Table 18. Samples are hypersaline but increase in salinity with depth. Salinity in the lowermost sample is slightly higher than that observed in the MMG groundwaters from Kirkham (Table 16). High salinity and high concentrations of Ca and SO_4 are consistent with gypsum and halite dissolution. By contrast, groundwater at shallower depth (206 m) in Sellafield No 2 borehole was fresh (Table 18).

3.8.3 East Lincolnshire

3.8.3.1 GROUNDWATER/POREWATER COMPOSITIONS

Oxford Clay Formation (OCF)

No data were available for groundwater/porewater in the OCF of east Lincolnshire. Proxies from locations in southern England have been taken as alternatives (Table 19). These are from depths up to 318 m but mostly much shallower.

All were squeezed porewaters except for groundwater samples from the “shallow” Elstow borehole (Table 19), summary data for which are cited in Ross et al. (1989) but without provision of sampling and analytical details. Original groundwater data for this site could not be accessed.

Porewater samples from the Harwell cores, Oxfordshire (Table 19) were extracted at BGS using a newly designed Ni-Cr-Mo alloy squeezing cell (Brightman et al., 1985). Samples of core material were preserved by wrapping in foil, sealing with wax and then refrigerated. They were opened, trimmed to remove the outer rim, cut and loaded to the squeezing cell under atmospheric conditions. Porewaters were squeezed under temperatures to simulate in-situ conditions (16–17°C). Porewater data indicated minimal moisture loss from the core following processing but oxidation of core was observed or inferred, affecting especially the speciation of S which was determined as SO_4 but may have been mixed SO_4/sulphide. A red-brown precipitate in the water samples also signified a production of Fe oxides on oxidation. Pyrite oxidation is inferred to account for the high concentration of measured SO_4 (14,600 mg/L) and the acidic pH (5.6).

The Harwell porewaters have the most saline composition observed (average of 6 analyses, Table 19, Figure 17) in the limited dataset for the OCF, and are from the greatest depth (224–318 m depth). The porewater from the Harwell boreholes is a Na-SO_4 composition. Brightman et al. (1985) inferred from head measurements that the hydraulic gradient in the OCF at Harwell was upward from the underlying Oolites towards the Corallian above.

Samples of porewater from Down Ampney, Gloucestershire (Table 19), were extracted to investigate the impacts of faulting on porewater movement and chemistry in the OCF, with boreholes located on either side of and within a fault zone (Metcalfe et al., 1990). Porewaters away from the fault were noted to be of Na-Cl type while those at the fault were dominated by Na-SO_4. Oxidation of pyrite, acid dissolution of carbonates and cation exchange were concluded to be influential processes (Metcalfe et al., 1990). Compositions of porewater and groundwater were noted to be similar, except for increased SO_4 concentrations in the former. Metcalfe et al. (1990) concluded that this may be due to oxidation of porewater during squeezing.

Shallow groundwater chemistry from Elstow area, Bedfordshire, reported by Norwest Holst (cited in Ross et al., 1989) (Table 19) has neutral pH and relatively low salinity, but with SO_4 concentration of 1380 mg/L, suggesting oxidation of sulphide. Porewater extracted from cores from two boreholes at Elstow (BB1, BB2) (at pressures up to 70 MPa; Table 19) (Ross et al., 1989) also had chemical compositions showing evidence of pyrite oxidation, with additional evidence for acid dissolution of carbonate minerals, equilibrium with respect to gypsum and cation-exchange reactions with clays.

Head data for the Elstow boreholes suggested the hydraulic gradient across the OCF was vertically downwards (Ross et al., 1989). The low salinity of the Elstow OCF porewaters suggests considerable flushing with fresh water since marine deposition of the sediments, a feature supported by stable-isotopic compositions of meteoric signature (Ross et al., 1989) (Figure 17). High concentrations of TOC in both the Elstow porewaters and groundwaters indicate the organic-rich nature of the OCF.

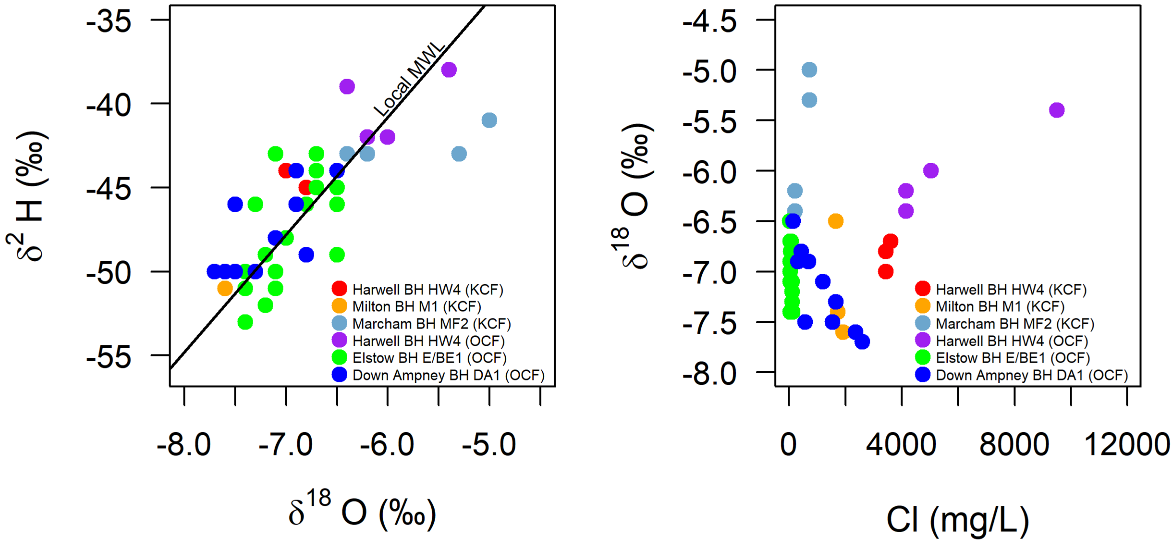

Figure 17. Stable-isotopic composition of porewaters extracted from Oxford Clay Formation (OCF) and Kimmeridge Clay Formation (KCF) boreholes of southern England. Local meteoric water line (MWL) from Darling and Talbot (2003); porewater data provided from Brightman et al. (1985), Ross et al. (1989) and Metcalfe et al. (1990).

Table 19. Summary water chemistry for the Oxford Clay Formation (OCF), southern and eastern England, mean values, concentrations in mg/L.

Location	Harwell, HW4, Oxon	Down Ampney, Gloucs	Elstow, Beds	Elstow, BB1, BB2, Beds
Type	PW	PW	GW	PW
Sample depth (m)	224–318	5–26	shallow	2.5–21.3
no. samples	6	13	13	5 (22*)
Ca	367	36.7	365	179
Mg	142	20.2	167	54.0
Na	5524	1090	528	344
K	73.4	5.93	34.4	10.4
Cl	5500	968	590	78.3
SO_4	14,569	687	1380	943
HCO_3	84	398	526	297
pH	5.6	8.3	7.13	8.0
Si	1.0	2.6	3.15	4.41
B	3.95			
Li	1.65			
Sr	14.0	2.5		6.34*
NO_3			<0.5	<0.5*
NH_4		0.95	<0.5	
Br		4.4		<0.25*
F		2.4		1.17*
Al			0.28	
TOC			54.1	27
Source	Brightman et al. (1985)	Metcalfe et al. (1990)	Norwest Holst (1988), cited in Ross et al. (1989)	Ross et al. (1989)

PW: porewater, GW: groundwater.

Kimmeridge Clay Formation (KCF)

Artefacts of sampling similar to the OCF porewaters are observed for porewaters from the KCF. The closest data to east Lincolnshire were found in the Harwell, Milton and Manor Farm (Marcham) boreholes, Oxfordshire (Brightman et al., 1985) and the Pickering borehole in North Yorkshire (Table 20). No data were found for offshore samples within 20 km of the coast.

For the Oxfordshire boreholes, porewater extraction was again carried out at BGS by squeezing in a purpose-built cell and compression rig with the core samples being prepared and extracted in air (at 12°C). Oxidation of the samples is again demonstrated in the Harwell core by the high concentration of SO_4 (3800 mg/L) and low mean pH (5.7) (Table 20). Porewater has a mean TDS of 11,300 mg/L and water is of Na-Cl-SO_4 type. Porewater solute concentrations are lower in the Oxfordshire cores from shallower depths, and the evidence for pyrite oxidation is weaker. Porewater TDS varies with core depth (Table 20). Na-Cl are the dominant ions. Brightman et al. (1985) concluded that head measurements in the Harwell boreholes were consistent with downward hydraulic gradient towards the Corallian, while the Milton and Manor Farm boreholes were consistent with upward hydraulic gradient and flushing of the KCF from the underlying Corallian aquifer. Flow was concluded to be dominantly advective.

For the Pickering site, core porewaters were squeezed at 18°C at the BGS Keyworth laboratory. Core was squeezed under N_2 in an attempt to minimise oxidation during processing. However, the high concentrations of SO_4 suggest that oxidation has occurred regardless. Porewater from shallow depths (27–60 m) has a mean TDS concentration of 10,600 mg/L and Na and SO_4 are the dominant ions (Table 20); pH was not determined in the extracted samples. Presence of minor amounts of pyrite have been recorded in the KCF at both the Harwell and Pickering sites, supporting the evidence for its oxidation. Average concentrations of DOC in groundwater from the borehole were 2.5 mg/L.

Table 20. Summary water chemistry for the Kimmeridge Clay Formation (KCF), eastern and southern England, mean values, concentrations in mg/L.

Location	Harwell, HW3/4, Oxon	Milton M2/1-5, Oxon	Manor Farm, MF2/7, Oxon	Pickering, N Yorks
Type	PW	PW	PW	PW
Sample depth (m)	163–179	34.2–54.5	6.7–13.7	27–60
no. samples	2	4	2	3
TDS	11,310	3485	973	10,600
Ca	271	21.4	20.0	179
Mg	68.0	13.8	7.5	58.6
Na	3570	1310	371	2970
K	35.6	12.2	4.90	15
Cl	3520	1780	473	317
SO_4	3840	127	96.0	6420
HCO_3	6.41	448		627
pH	5.7	8.6		
Si				4.4
B	1.2			3.24
Li	0.59	0.24	0.21	
Sr	12.5	1.06	0.72	10.2
Br				1.0
F				0.4
I				0.068
TOC				
Source	Brightman et al. (1985)	Brightman et al. (1985)	Brightman et al. (1985)	BGS archives

PW: porewater.

Mercia Mudstone Group (MMG)

For the MMG, no data were found offshore within a 20 km distance of the coast, and absence of available groundwater data onshore for east Lincolnshire has necessitated reporting of analyses from Retford, Nottinghamshire and Stow on the Wold, Gloucestershire (Table 21). For samples taken from depth <20 m (East Midlands), low solute concentrations are observed which suggests young groundwater (recent recharge) having interacted little with the host MMG. Nonetheless, concentrations of SO_4 are high where measured (average 300 mg/L), which could be derived from dissolution of gypsum. Here, derivation from pyrite is not inferred as the MMG is a relatively oxic, red-bed, deposit where pyrite is uncommon.

The groundwater sample from Stow on the Wold (Burley et al., 1984) is from greater depth (321 m); details of the sampling methodology are not given in the reference. The sample has a TDS of 1470 mg/L with relatively high concentrations of Na and SO_4 (Table 21).

Table 21. Summary water chemistry for the Mercia Mudstone Group (MMG), the Midlands and southern England, mean values, concentrations in mg/L.

Location	Retford, Nottinghamshire	Stow on the Wold 1, Gloucs
Type	GW	GW
Sample depth (m)	<20	321
no. samples	6	1
TDS	999	1470
Ca	166	122
Mg	47.1	20
Na	44.9	337
K	30.5	3
Cl	92.6	148
SO_4	300	822
HCO_3	317	44
pH	7.3	7.7
B	0.15	
Li	0.031	
Sr	1.17	
TOC		
Source	Smedley et al. (2018)	Burley et al. (1984)

GW: groundwater.

3.8.3.2 GROUNDWATER CHEMISTRY OF BOUNDING AQUIFERS

Chalk

Groundwater from the Chalk aquifer of east Lincolnshire and Yorkshire is unconfined in the western Wolds but becomes confined downgradient below Quaternary deposits. Unconfined Chalk and much of the confined Chalk contains fresh groundwater of Ca-HCO_3 composition. In coastal areas, salinity increases and saline zones are noted in the Holderness Peninsula, Humber Estuary and Grimsby area. In east Lincolnshire, groundwater concentrations of Cl up to 1100 mg/L and SO_4 up to 130 mg/L were reported by Smedley and Brewerton (1997). In Yorkshire, highest observed concentrations of Cl and SO_4 in groundwater at the eastern limit of the flow path are 8900 mg/L and 1290 mg/L respectively (Smedley et al., 2004). Due to its high salinity, this groundwater has been selected as an appropriate chalk end member (Table 22). The saline zones are considered to have been caused by influxes of various generations of seawater (Edmunds et al., 2001a), the oldest in the Holderness Peninsula and south Lincolnshire which likely derive from Ipswichian interglacial saline intrusion (Edmunds et al., 2001a; Hiscock and Lloyd, 1992). A sample from 80 m depth in the confined Chalk aquifer from Atwick, north of Hornsea, also has a reported Cl concentration of 5840 mg/L (Elliot et al., 2001).

Spilsby Sandstone

Groundwater from the Lower Cretaceous Spilsby Sandstone of Lincolnshire is freshwater, even in the near-coastal zone, and forms a local drinking-water supply (Edmunds et al., 2001a). A groundwater Cl concentration of 210 mg/L and SO_4 concentration of 78 mg/L is recorded at the easternmost extent of the aquifer (Table 22).

Sherwood Sandstone Group

Chemistry of groundwater in the deep confined Sherwood Sandstone of the East Midlands is shown from two boreholes in the confined section of the aquifer in Lincolnshire (Table 22). Groundwater salinity remains relatively low in the Yawthorpe borehole groundwater, although concentrations of SO_4 increase due to dissolution of gypsum/anhydrite. This could be due to reaction within the Sherwood Sandstone or to interactions with evaporites at the interface with the overlying MMG. Sulphur isotopic data suggest that some sulphate reduction has occurred in this deep section of the aquifer, in contrast to further upgradient where SO_4 reduction was not considered a significant process (Smedley and Edmunds, 2002). At the Welton location (Table 22), groundwater salinity is higher due to presence of old trapped saline water at depth. Oxygen and deuterium stable isotopic compositions of these two groundwaters are depleted ($\delta^{18}O$ -8.6 ‰ and -8.9 ‰ and δ^2H -62 ‰ and -60 ‰ for Welton and Yawthorpe respectively), suggesting a meteoric water origin of pre-Holocene age.

Porewater chemistry of the confined Sherwood Sandstone at depth was also reported for the Cleethorpes No 1 geothermal borehole by Downing et al. (1985). Chloride concentrations were in the range 18,000–44,000 mg/L and SO_4 in the range 3180–3940 mg/L from the three representative porewaters listed in that report (Table 22). Compositions of δ^2H in the three samples were in the range -46 to -49 ‰ and concluded to be of meteoric water origin (Downing et al., 1985). The salinity of these porewaters was noted to be only quarter to half that of groundwater found in the Sherwood Sandstone of the Wessex Basin (boreholes at Marchwood, Southampton, Winterbourne Kingston) (Downing et al., 1985).

Table 22. Summary groundwater chemistry for individual groundwater samples from aquifers in eastern and north-east England (Chalk of east Yorkshire, Spilsby Sandstone of Lincolnshire, Sherwood Sandstone of Lincolnshire), concentrations in mg/L.

Location	Chalk, east Yorks	Spilsby Sandstone, Lincs	Sherwood Sandstone, Yawthorpe, Lincs	Sherwood Sandstone, Welton, Lincs	Sherwood Sandstone, Cleethorpes No 1, 84/260 Lincs	Sherwood Sandstone Cleethorpes No 1, 84/266, Lincs	Sherwood Sandstone Cleethorpes No 1, 84/271, Lincs
Type	GW	GW	GW	GW	PW	PW	PW
Sample depth (m)		110	406	804	1113	1204	1306
TDS	16,600	1110	1980	10,130	35,300	56,300	80,200
Ca	250	1.8	353	1200	1170	2170	2080
Mg	630	1.3	108	291	326	467	558
Na	4,910	338	62.6	2030	11,700	18,800	28,400
K	155	5.6	12.5	38.31	123	670	2150
Cl	8900	210	22.1	5000	18,200	30,200	43,600
SO_4	1290	78.3	1330	1500	3180	3940	3310
HCO_3	430	475	96	73.2			
pH	7.2	8.7	7.91	7.93			
Si	2.3	3.2	4.6	6.0			
B	2.2	0.82	0.13	0.19		0.81	
Sr	27	0.16	5.26	25.9			
F	3.8	2.3	0.1	0.02			
TOC							
Source	Smedley et al. (2004)	Edmunds et al. (2001a)	Smedley and Edmunds (2002)	Smedley and Edmunds (2002)	Downing et al. (1985)	Downing et al. (1985)	Downing et al. (1985)

PW: porewater, GW: groundwater.

3.8.4 East Anglia

3.8.4.1 GROUNDWATER/POREWATER COMPOSITIONS

Mercia Mudstone Group (MMG)

A single analysis from a groundwater (sample depth 683 m) in the MMG of Norfolk is shown in Table 23. This is an old analysis with limited amounts of background information, including the sampling and analytical methodology (Burley et al., 1984). However, the depth of the sample makes it an analysis of particular interest. The water is saline and Na-Cl dominant.

Table 23. Summary water chemistry for the Mercia Mudstone Group (MMG), Norfolk, concentrations in mg/L.

Location	Somerton No 1
Type	GW?
Depth (m)	683
TDS	52,400
Ca	3000
Mg	800
Na	16,700
K	240
Cl	31,000
SO_4	580
HCO_3	200
pH	7.1
TOC	
Source	Burley et al. (1984)

GW: groundwater.

3.8.4.2 GROUNDWATER CHEMISTRY OF BOUNDING AQUIFERS

Chalk

The Chalk of northern East Anglia is dominantly a freshwater aquifer, used for regional water supply (Table 24). Shallow Chalk groundwater from the area of the Great Ouse catchment is dominantly oxic, pH-neutral fresh recharge, of Ca-HCO_3 type reflecting carbonate reactions. Concentrations of nitrate are commonly high and indicate the influence of dominantly agricultural pollution in this rural catchment (Ander et al., 2004). Quaternary till deposits over parts of the East Anglian Chalk (interfluve areas) and Crag to the east of East Anglia provide confining and mildly reducing (Fe-, Mn-) conditions, albeit still in dominantly fresh groundwater.

By contrast to these fresh waters, porewaters extracted by centrifugation from Chalk core material at Trunch, Norfolk were of saline composition (Bath and Edmunds, 1981). The porewaters showed depth-dependent increase in salinity in core extending from 80–500 m depth (Table 24) which at the base of the Chalk sequence resembled seawater in its Na-Cl content, albeit with a slightly depleted $\delta^{18}O$ and $\delta^{2}H$ isotopic character (-3.7 ‰ and -23 ‰ respectively at seawater salinity). The saline water was taken as a mix of connate water (i.e. seawater that has a very long residence time and is possibly relict from deposition of the Chalk during the Cretaceous) with fresh recharge. The age of the saline end member was subsequently contested by Heathcote and Lloyd (1984) who suggested that this could be Crag (Pleistocene) seawater which flushed the Chalk during the later Quaternary (Heathcote and Lloyd, 1984).

Sandringham Sands

The Lower Cretaceous marine Sandringham Sands of Norfolk overlie disconformably the KCF (Casey and Gallois, 1973). These also contain fresh groundwater which form public and private supplies of water locally (Table 24). The groundwater in the Sandringham Sands is not known to be old water, but is mildly reducing with overal low concentrations of NO_3 and increased concentrations of dissolved Fe (average 2.3 mg/L; Table 24). The Sandringham Sands are approximately contemporaneous with the Spilsby Sandstone of Lincolnshire and are confined by the overyling units of the Lower Cretaceous.

Table 24. Summary water chemistry for the aquifers of East Anglia: Chalk and Sandringham Sands, concentrations in mg/L; *estimate based on summation.

Location	Chalk, Thetford, Norfolk	Trunch, Norfolk	Trunch, Norfolk	Sandringham Sands, Norfolk
Type	GW	PW	PW	GW
Sample depth (m)		115	500	
no. samples	5	1	1	7
TDS	640	2920*	36,000*	695
Ca	99	85	650	95.9
Mg	2.16	103	1280	3.4
Na	12.0	910	11,000	11.5
K	1.94	33	282	1.90
Cl	22.6	1410	19,700	19.1
SO_4	20.3	350	3060	23.8
HCO_3	235			270
NO_3-N	8.64			<0.1
pH	7.13			7.10
Sr	0.278	28	20	0.299
F	0.16	3.5	1.9	0.10
Fe				2.30
TOC				
Source	Ander et al. (2004)	Bath and Edmunds (1981)	Bath and Edmunds (1981)	BGS archives

PW: porewater, GW: groundwater.

3.8.5 Wessex Basin

3.8.5.1 GROUNDWATER/POREWATER COMPOSITIONS

Kimmeridge Clay Formation (KCF)

There exists also a paucity of data for groundwater from the KCF in the Wessex Basin. Analyses of two groundwater samples taken from a borehole in the Ashdown area of east Sussex are shown in Table 25. These were collected during drilling operations for installation of an observation borehole. As such, they are unlikely to be representative of steady-state in-situ conditions. Nonetheless, they likely provide some sense of the salinity of groundwater at the depths sampled. The compositions indicate TDS values of 22,000–36,000 mg/L, i.e. up to seawater salinity, with NaCl as the dominant ions; pH is near-neutral to slightly alkaline. Alkalinity (as HCO_3) is high (770–1010 mg/L), likely reflecting oxidation of organic carbon and dissolved CH_4. Such alkalinity values are not atypical for groundwater from the KCF (Smedley et al., 2017).

Limited data for a groundwater sample from Steeple Ashton, Wiltshire, from much shallower depth, indicates lower salinity but still with a Cl concentration of 2750 mg/L (Table 25). Sampling information for the site is not available but the analysis dates from 1928 which explains the limited number of analytes.

Table 25. Summary groundwater chemistry for the Kimmeridge Clay Formation (KCF), southern England, concentrations in mg/L.

Location	Ashdown, Sussex	Ashdown, Sussex	Steeple Ashton, Wilts
Type	GW	GW	GW
Sample depth (m)	629	702	38
TDS	35,700	22,200	5240
Ca	404	200	
Mg	12	12	
Na	13,500	8820	
K	23	34	
Cl	20,590	13,000	2750
SO_4	781	592	
HCO_3	770	1010	
pH	7.4	7.8	
TOC			
Source	BGS archives	BGS archives	BGS archives

GW: groundwater.

Oxford Clay Formation (OCF)

Regarding groundwater from the OCF of southern England, the only analysis that could be accessed is from a borehole in Didcot, Oxfordshire (Table 26). The borehole is shallow (105 m deep) but with a high TDS of 11,000 mg/L and a NaCl composition. Little information is available for the sample but the data are presented in Burley et al. (1984).

The organic-rich nature of the OCF sediments is well-established (Hudson and Martill, 1991). Within the Wessex Basin, investigation for hydrocarbon gases by total-gas logging in the Southampton No. 1 geothermal borehole found higher concentrations (750 ppm, 0.075% total gas, at 927 m depth) than in any other lithology of the borehole which penetrated the whole Jurassic sequence and extended down as far as the Sherwood Sandstone (Thomas and Holliday, 1982).

Table 26. Composition of a sample of groundwater (of unknown depth) from the Oxford Clay Formation (OCF), southern England, concentrations in mg/L.

Location	Didcot Ordnance Depot, Oxon
Type	GW
Depth (m)	Borehole: 105
TDS	10,800
Ca	283
Mg	205
Na	2860
K	
Cl	5720
SO_4	1595
HCO_3	122
pH	
Si	25.7
TOC	
Source	Burley et al. (1984)

GW: groundwater.

3.8.5.2 GROUNDWATER CHEMISTRY OF BOUNDING AQUIFERS

Chalk

Rocks of Upper Jurassic and Lower Cretaceous age overlie the KCF of southern England (Figure 7) which are in turn overlain by the Chalk. As such, the Chalk is not a bounding aquifer to the KCF but it does provide comparatively rich information on the composition of groundwater in this shallow major aquifer of the region.

Chemistry of groundwater in the Wessex Basin has been summarised by Allen and Crane (2019) (Table 27). The Chalk aquifer is important for regional water supply and is dominantly fresh. Groundwater is unconfined in some areas of the Wessex area Chalk (e.g. Purbeck Hills, Lulworth, Frome and Piddle catchments) but confined below Palaeogene deposits in others (Wareham, Poole Harbour) (Edmunds et al., 2002). Groundwater chemistry reflects the impacts of redox processes between the confined and unconfined sections and increasing contributions of Na and Cl towards the coast. Unconfined sections are fresh but contaminated by modern agricultural pollution (NO_3). Confined sections likely contain groundwater of pre-industrial age and not influenced by modern pollutants (Table 27) (Edmunds et al., 2002).

Table 27. Chemical compositions of groundwater in the Chalk aquifer of the Wessex Basin, mean values where multiple, concentrations in mg/L.

Location	Regional Chalk groundwater, Wessex Basin	Confined Chalk groundwater, Stoborough
Type	GW	GW
TDS	300	373
no. samples	>100	1
Ca	101	60
Mg	3	17.2
Na	14	63
K	1.5	3.3
Cl	23	85
SO_4	17	8
HCO_3	274	277
NO_3-N	5.6	<0.1
pH	7.38	7.5
DO	7.8	<0.1
Si	5.5	
F	0.237	
B	32	
TOC		
Source	Allen and Crane (2019)	Edmunds et al. (2002)

GW: groundwater.

Groundwater samples from three boreholes in the confined Chalk west of Poole Harbour (Bulbury (60–90 m depth), Lytchett Minster (65–110 m depth) and Holton Heath (120–250 m depth)) showed a general slight increase in Na and Cl contents with depth (Na: 10–180 mg/L; Cl: 20–180 mg/L), both within and between these sites. Stable-isotopic compositions were consistent with a Holocene age for the deepest of these groundwaters, with evidence of increasing water-rock interactions, including ion exchange, at the greatest depths (Allen and Crane, 2019). Groundwaters in the confined section of the aquifer at Poole Harbour were interpreted to be up to 20,000 years old and therefore of Pleistocene age (Edmunds and Shand, 2008). During this period and to around 8000 years ago, sea levels would have been lower than the present level (-115 m) due to glacial/periglacial climate and expansion of ice caps. Base levels of erosion and groundwater flow during the Pleistocene would have been lower than current levels with potential for flushing of the Chalk aquifer with fresh recharge. Freshwater to the base of the Chalk aquifer has been described at the south coast of Dorset (Edmunds and Shand, 2008). Some indication of freshwater (SEC estimated as <10 mS/cm) within the underlying Greensand aquifers has also been reported for this area (Edmunds et al., 2001b).

Sherwood Sandstone Group

The Sherwood Sandstone underlies the MMG in the Wessex Basin with the interface at depths of some 800 m to over 2000 m. The groundwater in the Sherwood Sandstone at such depths is hypersaline. Data for groundwater from the deep Sherwood Sandstone (top at some 1700 m depth) in the Marchwood and Western Esplanade low-enthalpy geothermal boreholes in Southampton show TDS concentrations of 103,000 and 125,000 mg/L (specific electrical conductance 131 and 155 mS/cm) respectively (Allen et al., 1983; Thomas and Holliday, 1982) (Table 28). In these boreholes, relatively low dissolved CH_4 concentrations were found: around 5.5 mg/L and 7.8 mg/L respectively (Darling and Gooddy, 2006).

Table 28. Chemical compositions of brine from the deep Sherwood Sandstone Group in low-enthalpy geothermal boreholes from Southampton, concentrations in mg/L.

Location	Marchwood	Western Esplanade
Type	GW	GW
TDS	103,370	124,590
Ca	3670	4240
Mg	658	752
Na	33,240	41,300
K	582	705
Cl	63,815	75,900
SO_4	1400	1230
HCO_3	81	71
pH (surface)	6.75	6.0
Eh (mV)	-300	-200
Si	15.5	17.8
TOC		
Source	Downing et al. (1983)	Downing et al. (1983)

GW: groundwater.

3.8.6 Clay porewater analogues

Besides the LSSRs listed in the project plan, an evaluation has been made of other LSSRs in the UK as well as elsewhere in Europe. This is for the purposes of comparison with the LSSRs described above and to gather extra data of potential value to characterisation of their variability. The rock types investigated are the Lias Group of eastern England, the Callovo-Oxfordian Clay of Bure, France and the Opalinus Clay of Switzerland.

3.8.6.1 LIAS GROUP, EASTERN ENGLAND

The Lower Jurassic Lias Group is an organic-rich marine mudrock with siltstones and occasional limestones. In the cored Trunch borehole in Norfolk, two samples of porewater were extracted from Lias Group clays below the Chalk. These porewaters had Na contents lower than that from the lowest parts of the Chalk, although Cl content was slightly greater than seawater (24,000 mg/L) and comparable with the Chalk porewater compositions (Bath and Edmunds, 1981) (Table 29). Presence of an old, yet of unknown age, seawater component is apparent in the Lias at this location. These porewater compositions are for the depth range of interest in comparable LSSR host rocks.

Porewaters in Lias siltstones, clays and limestones at shallow depth from three cored boreholes in Fulbeck, Lincolnshire were described by Bath et al. (1989). Core was stored for some weeks before processing and only one sample was extracted under anaerobic conditions (Bh31, 20.15 m depth) so some storage and processing artefacts are likely. The porewaters have relatively low solute concentrations but with evidence of Na-Cl concentrations increasing with depth (Bh31 and Bh32, Table 29). Bath et al. (1989) inferred this to be related to the presence of older relict brackish porewater in the deeper part of the profile and therefore lack of fluid movement. Porewater from the Fulbeck cores appears to be anoxic, with detectable dissolved Mn and Fe(II), the redox conditions probably driven by organic carbon, as suggested by high porewater TOC concentrations (Table 29). High concentrations of SO_4 suggest that water samples have undergone pyrite oxidation, either in situ or during processing, and alkaline pH may be a function of degassing of CO_2 during the extraction or reaction of carbonate from the limestone or clays in situ.

Table 29. Chemistry of porewater in the Lias Group, eastern England, concentrations in mg/L.

Location	Trunch	Trunch	Bh29 Fulbeck	Bh31 Fulbeck	Bh31 Fulbeck	Bh32 Fulbeck	Bh32 Fulbeck	Bh32 Fulbeck	Bh31 Fulbeck
Type	PW	PW	PW	PW	PW	PW	PW	PW	PW
Lithology	clay	clay	FLst	FLst	BC	Obt	FLst	BC	FLst
Depth (m)	530	594	22.3	6.95–24.7	32–37.9	5.15	11.15–25.15	35.15–44.55	20.15
No. samples	1	1	1	7	3	1	3	3	1
Ca	1130	1080	7.6	107	42.0	6.8	32.3	245	210
Mg	930	560	2.4	65	38	1.9	20.8	160	130
Na	10,850	8350	968	1980	2247	177	1680	4110	3200
K	323	252	5.9	13	4.8	3.0	6.8	20	13.2
Cl	23,700		840	397	1927	42	351	1687	206
SO_4			636	3536	2073	259	3290	7343	7990
HCO_3			200	356	287	125	510	352	183
pH			7.8	7.5	7.9	9.1	8.3	7.5	7.43
Sr	37	28	0.30	7.26	4.23	0.20	2.63	18.4	16.9
Ba			0.030	0.055	0.032	0.010	0.025	0.043	0.083
Si			2.1	4.2	3.5	1.9	2.8	3.0	3.2
Mn			0.190	0.626	0.423	<0.01	0.057	0.627	0.48
TOC				41	97	15	27	57	73.2
NH_4									4.6
Fe_T									1.49
Fe(II)									0.156
Al									<0.05
U									0.34
Source	Bath and Edmunds (1981)	Bath and Edmunds (1981)	Bath et al. (1989)	Bath et al. (1989)	Bath et al. (1989)	Bath et al. (1989)	Bath et al. (1989)	Bath et al. (1989)	Bath et al. (1989)

PW: porewater, FLst: Ferruginous Limestone, BC: Bucklandi Clay, Obt: Obtusum Oxynotum Clay.

A high concentration of U (0.34 mg/L) in one Lias porewater sample was inferred to be potentially due to presence of traces of a phosphate mineral in the core (Bath et al., 1989). The water sample may contain some colloidal material as suggested from the discrepancy between Fe_T and Fe(II) concentrations. An alternative explanation for the presence of U may be as a species adsorbed to colloidal Fe and/or organic matter. Uranium was only measured in one sample so there is no indication of how representative this observation is.

Callovo-Oxfordian Clay, Bure, France

The English OCF is penecontemporaneous with the Callovian-Oxfordian (COX) clay rocks studied in detail in a repository context at the Bure Underground Research Laboratory (URL), East Paris Basin (Gaucher et al., 2006; Gaucher et al., 2009). The ANDRA facility has a main gallery at 490 m depth within the 130 m thick COX formation. Units are clay dominant in the lower part, with more silt higher in the sequence and greater content of carbonate in the top part (Gaucher et al., 2006). The clay-dominant zone occurs in the approximate 417–489 m depth range and initial experiments were conducted at depths of 445 m and 490 m, with other core material added for investigation subsequently (Gaucher et al., 2009).

A comprehensive approach to porewater characterisation has been undertaken, including core analysis, modelling and in-situ porewater sampling. Core samples of COX clay material had a water content in the range 6–9% (dry wt). Core investigations of CO_2 partial pressure at depths around 420–480 m measured by gas chromatography were in the range $10^{-2.9}$ to $10^{-2.4}$ bar and $\delta^{13}C$ isotopic compositions of dissolved inorganic carbon (DIC) in equilibrium with the gas in the range -2 to +2 ‰, consistent with its control by reaction of carbonates rather than with organic matter or influx from other formations (Gaucher et al., 2006). Concentrations of SO_4 in the COX of the Paris Basin are likely controlled by celestite solubility (Gaucher et al., 2009; Wersin et al., 2017).

Gaucher et al. (2006) modelled the chemistry of porewater in the COX assuming thermodynamic equilibrium with the minerals in the formation. High-temperature or high-pressure detrital phases were deliberately not considered (Gaucher et al., 2009). Deriving the model composition involved modelling the dilution of seawater with pure water and then modelling equilibration with host minerals in contact with porewater in the Bure system (quartz, calcite, dolomite, siderite, celestite, daphnite, pyrite ±Mg-chlorite and ion exchange on clays). Modelled in-situ Cl concentrations took account of geochemical porosity (Section 3.7). Given uncertainty in the ambient porewater pCO_2 values, a range of pCO_2 scenarios was considered by Gaucher et al. (2006). Model data for a scenario using the mid-range of measured pCO_2 values (i.e. $10^{-2.51}$ bar) in the study area (scenario “B”) are given in Table 30.

An alternative method of extraction of porewaters involving outgassing of core material in inert He or Ar was developed to improve estimation of dissolved gases (Lassin et al., 2016). This, combined with analysis of stable C isotope values, Gaucher et al. (2010) allowed what were considered more reliable pCO_2 values to be derived. Lassin et al. (2016) confirmed from experiments that the COX porewater pCO_2 values ranged between $10^{-3.0}$ and $10^{-2.0}$ bar, but that an important controlling factor is relative humidity (degree of saturation) of the clay material. The range of pCO_2 values was comparable with the range from the earlier studies cited in Table 30. The C isotopic data suggested that the carbonate system is regulated by the presence of calcite, dolomite and chlorite-type Mg clays (Gaucher et al., 2010).

Table 30. PHREEQC modelled results for porewater composition in the Callovo-Oxfordian of Bure, East Paris Basin (using the llnl.dat thermodynamic database): compositions are according to scenario “B” (pCO_2 value taken as $10^{-2.51}$ bar, within the middle of the observed range; density taken as 1.002 g/cm^3); (molal data from Gaucher et al., 2006). Experimental COX porewater data taken from data for borehole PAC1001 in a water circulation experiment for 287 days’ reaction time (Vinsot et al., 2008). Modelled data for the PAC1001 borehole also shown (Appelo et al., 2008). pCO_2 values are consistent with those given by Lassin et al. (2016). Concentrations in mg/L unless otherwise stated.

Location	Modelled COX porewater, Bure (scenario “B”)	Experimental COX porewater, Bure, PAC1001, 287 days	Modelled results for porewater from PAC1001
Depth (m)	400–540	505	505
pCO_2 (bar)	$10^{-2.51}$	$10^{-2.1}$	$10^{-2.0}$
pH	7.28	*7.4	7.1
Eh (mV)	-176	-199	-200
TDS	6400	4160	4950
Alkalinity (HCO_3)	79	212	275
Cl	1070	1241	1666
SO_4	3273	1201	1345
S as S	–	3.1	
Na	738	1051	1241
K	277	24.4	25.4
Ca	595	202	261
Mg	344	105	122
Sr	98	16	17
Si	2.66	3.93	
Al	0.00023		
Fe	5.3		
Li		0.52	
Source	Gaucher et al. (2006)	Vinsot et al. (2008)	Appelo et al. (2008)

*lab measurement.

Vinsot et al. (2008) subsequently reported results from field water-circulation experiments carried out at the Bure site. Table 30 shows results for circulation experiments after 287 days in borehole PAC1001 at 505 m depth. Reported porewater compositions are also given from modelling results reported by Appelo et al. (2008). These were taken by Vinsot et al. (2008) to be the best estimates for the porewater chemical composition in the COX at 505 m depth at the Bure site. The Vinsot et al. (2008) results are broadly comparable with those of Appelo et al. (2008).

In work carried out by Gaucher et al. (2009), discrepancies between the Gaucher et al. (2006) modelled results and the experimental data acquired by Vinsot et al. (2008) for K, SO_4 and Sr (Table 30) were resolved by improving sampling technique (e.g. use of N_2 for core preservation to minimise oxidation) and improved model parameters which reduced the impacts of pyrite oxidation on dissolved SO_4 concentrations, reduced dissolution of celestite, and reduced the resultant impact on exchangeable cation distributions.

3.8.6.2 OPALINUS CLAY, MONT TERRI, SWITZERLAND

The Opalinus Clay is a consolidated marine mudrock of Middle Jurassic age (Aalenian, 180 Ma) and the host for investigations in the context of radioactive waste disposal at the Mont Terri URL in Switzerland. The Mont Terri Tunnel intersects a 245 m section of the Opalinus Clay which has an apparent thickness of 160 m and dips at an angle of 30–40° to the south-east in the limb of an anticline (Fernández et al., 2013; Pearson et al., 2003). The maximum overburden above the URL is about 300 m.

Porewaters were collected by squeezing of Opalinus Clay core samples from holes drilled from the Mont Terri URL (Table 31) (Fernández et al., 2013). The porewaters were concluded to be representative of in-situ porewater compositions, without significant artefacts from squeezing (membrane effects), as they were squeezed under optimised pressures (≤200 mPa) and also resembled local in-situ porewaters extracted from packered sections of boreholes in the same rock unit.

The porewater in the Opalinus Clay is a saline Na-Cl water. The Br/Cl and SO_4/Cl ratios have been noted to resemble seawater signatures, albeit with some variability (Pearson et al., 2003). Stable water isotope compositions have been inferred to indicate presence of a partially evaporated seawater (Mazurek and de Haller, 2017; Pearson et al., 2003). Compositions are more enriched than regional modern groundwater (Rübel et al., 2002).

Table 31. Porewater samples extracted from Opalinus Clay core material by squeezing (Fernández et al., 2013), concentrations in mg/L.

Borehole	BHT-1	BDR-2	BWS-E6	BWS-A6	BWS-A4	BWS-A5	BWS-E4
Depth (from tunnel wall, m)	12.42–12.96	5.93–6.96	3.05–3.40	4.1–4.3	6.99–9.94	7.40–7.79	4.28–4.65
no. samples	6	1	1	1	2	4	1
pH	6.7	7.3	6.8	6.9	7.25	7.2	8.1
TDS	18,640	11,510	20,450	21,930	21,685	23,290	7700
Cl	9900	6100	11,000	12,000	9,500	11,000	2500
SO_4	1967	1300	1500	1700	4150	3800	2500
Br	29.8	19.5	34	35	34.5	36	7.0
NO_3	10.1	3.4	1.6	4	3	4.2	11
Alk (HCO_3)	2.7	1.5	98.2	nd	61.1	362	
SiO_2	6.9						
Na	5450	3300	6450	6200	5950	6550	2100
K	43.3	20	60	69	88.95	70	48
Ca	647	465	665	925	1113	790	235
Mg	534	247	595	950	730	620	255
Sr	44	50	45	46	54	56	45
Fe	0.6	0.3					
Al	0.33	0.15					
B	6.1	3.3					
Ba			0.2	0.44	0.41	0.2	<0.3

In a study summarising 20 years' research at the Mont Terri laboratory, Mazurek and de Haller (2017) outlined the evolutionary history that gave rise to the Opalinus' porewater chemistry. Opalinus Clay was deposited in the Middle Jurassic in open marine basinal conditions which following diagenesis became reducing, with evidence of SO_4 reduction and subsequent precipitation of pyrite. Inversion in the late Cretaceous established a change from marine to continental conditions, with erosion, karstification of overlying limestones and downward movement of fresh water to flush the Jurassic marine clays. Geochemical modelling results led to an inference of porewater salinity of the Opalinus Clay diminishing to half its original value by the end of the Palaeogene. Marine incursion at around the end Oligocene/early Miocene (23 Ma) and subsequent evaporation of surface seawater led to the formation of gypsiferous deposits and diffusion of brine into the limestones with a slow diffusive resalination of the underlying Opalinus porewater. Reestablishment of freshwater conditions at surface, together with erosion, led to reactivation of freshwater aquifer flow and a further partial freshening of the clay porewaters in the uppermost Miocene at around 9–4 Ma to produce their current compositions. The porewaters at Mont Terri and nearby Mont Russelin have curved vertical profiles for inert tracers (Cl, Br, stable oxygen and deuterium isotopes) that cannot be explained by simple binary mixes of seawater and meteoric water (Pearson et al., 2003). Porewater data extracted by direct sampling from closed boreholes, squeezing and leaching were considered reliable for most major ions and stable isotopes, while porewater degassing meant that data for carbonate equilibria including pH and pCO_2 were considered less reliable.

Further data for Mont Terri and Mont Russelin Opalinus Clay porewater are summarised in Table 32 (after Mazurek and de Haller, 2017). Data are comparable with those given by Fernández et al. (2013). Investigations by Pearson et al. (2011) found that best modelling results for the Opalinus Clay were achieved by assuming equilibrium with the minerals calcite, dolomite, siderite and daphnite, as well as Na-K-Ca-Mg exchange and/or kaolinite, illite, quartz and celestite equilibrium. Inclusion of detrital feldspar was not considered important.

Table 32. Data for porewater from the Opalinus Clay of Mont Terri URL and Mont Russelin. Data are from Mazurek and de Haller (2017) and references therein, and from Mäder (2009), concentrations converted to mg/L.

Location	Mont Terri BWS-A1	Mont Terri BWS-A2	Mont Terri BWS-A3	Mont Terri BWS-H2	Mont Terri BPC-C	Mont Terri BBB3	Mont Terri Ref GW	Mont Russelin deep ground-water
Ca	570	43	283	455	774	547	505	
Mg	344	311	151	286	542	370	236	
Na	5610	4315	2864	4430	6414	4880	3806	
K	65.3	130	40.6	51.8	69.6	59.5	102	
Cl	10,395	6067	4909	7420	11,628	8230	5712	18,400
SO_4	1251	1903	1082	1050	1651	1480	2390	
F	0.77	0.17	0.47	0.8				
Sr	35.5	2.2	31.6	40.1	42.9		18.6	
Br	36.3	23.9	15.2	27.1		23.6		65
Sources	Pearson et al. (2003)	Pearson et al. (2003)	Pearson et al. (2003)	Mazurek and de Haller (2017)	Vinsot et al. (2008)	Mazurek and de Haller (2017)	Mäder (2009)	Mazurek and de Haller (2017)

4 Concluding remarks

The characteristics of LSSRs and evaporites considered suitable for disposal of radioactive waste material have become clear from numerous national and international studies (e.g. Savage, 1996). These include reducing conditions, near-neutral pH, capacity for cation exchange on clays, retarded diffusive flux of anions (e.g. ^{129}I) (Gaucher et al., 2009) and retarded transport of all radionuclides.

The data gathering carried out for this investigation has highlighted the paucity of available porewater/groundwater data, the often ad-hoc, experimental or opportunistic nature of past sampling, and therefore the considerable uncertainties that exist for porewater compositions in specific rock types from specific areas and at specific depth ranges of interest.

Even where data do exist, the challenges of extracting undisturbed porewater from consolidated low-permeability clays, including the LSSRs described in this guide, are immense. The extraction (most commonly by squeezing at high pressures in the case of the English clays) can acquire porewater but has considerable potential to introduce sampling artefacts, including oxidation, mineral and surface reactions, microbial reactions and changes in gas pressures. The small water content and the strong interactions with clays are key factors in increasing uncertainty and inducing changes on sampling. Squeezing pressures can also impact on the origin of the water extracted, which is distributed between free porewater, adsorbed water in the clay double layer and strongly adsorbed interlayer water in the clay mineral structure.

As a result of the difficulties, international research effort has focused largely on experimental studies and geochemical modelling, conducted in or for defined field laboratories (e.g. Bure, Mont Terri). Data acquisition has included more diverse porewater extraction methodologies besides squeezing, such as leaching, advective displacement, and sampling from dedicated boreholes under controlled conditions (Gaucher et al., 2009). Use of multiple methodologies of investigation for some of the experiments, including leaching, squeezing, advective displacement and extraction from dedicated boreholes, have produced extra, sometimes redundant, analytical results (Vinsot et al., 2008; Wersin et al., 2017). This multiple approach is favourable to a good understanding of the data and its reliability. Consistency of multiple lines of data also helps to build confidence in the quality of analytical results. The combinations of data can be used in a coherent thermodynamic model to gain a clear understanding of the equilibria that control the porewater chemistry.

To progress knowledge on porewater/groundwater chemical composition in UK LSSRs, dedicated and carefully designed studies will be undertaken in support of the siting process, and as it develops. Data acquired for this guide provide a tentative first step towards this process. However, much of the information provided highlights the problems more than the potential improved knowledge. Robust datasets will be obtained via detailed field investigations, with extraction and interpretation of porewater/groundwater evolutionary history from multiple lines of evidence. New studies need to maintain cognisance of the challenges in providing reliable data. Investigations of porewater composition need to consider a broader suite of analytes than the mainly major ions considered in this guide, in order to provide the necessary underpinning data for design, permitting ultimate delivery of a GDF.

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Appendix 1 Groundwater/porewater data collection methodology

Data are provided for groundwater/porewater compositions for the four rock types of interest. Collated data were assigned qualitative ratings for relevance and confidence in order to evaluate their potential reliability. The relevance ratings assigned were low or high. A low relevance rating was assigned to data derived from groundwaters or porewaters from a depth of <200 m. A high relevance rating was assigned to data derived from groundwaters or porewaters from within the agreed depth range of 200–1000 m. Data are provided in Appendix 3.

Confidence in the data was based on a number of considerations:

- how recent are the data? Older data were given lower confidence ratings owing to improvements in analysis techniques over the years;
- does the procedure used by the analysing laboratory have UKAS accreditation? Accreditation is likely to be associated with newer data, and adds an extra level of confidence in the analyses;
- analysis units: data presented in an obsolete unit (e.g. grains per gallon) are older and were given lower confidence ratings to account for potential rounding errors of original data;
- sampling technique: a flowing groundwater sample, for example, would be more representative of groundwater in situ than a grab sample from a borehole;
- unclear depth: where data were obtained from original borehole logs, some of which were very old, there was occasionally some uncertainty in the depth of the sample. Where it was most likely the sample was within the rock type of interest the confidence level of the analyses was lowered. Where it seemed more likely the analyses represented other strata they were not included in the database.

There were a number of other reasons to lower the confidence ratings which were individual to a specific analysis or report. These were:

- a report in which it was suggested that a groundwater was derived from the Sherwood Sandstone Group but subsequent independent investigation identified borehole collapse and blockage such that groundwater accessed was likely from the MMG;
- a table in a report not stating the units of measurements. These were assumed to be the same as reported elsewhere in the report, but such an omission introduced a level of uncertainty.

The above considerations were taken into account when applying a rating for the data confidence. As there were many potential variables, the qualitative sample ratings were given on a scale of extremely low to high. Both relevance and importance ratings should be taken into account in evaluating the reliability of individual analyses.

Appendix 2 Spatial distribution of rock types of interest

KIMMERIDGE CLAY FORMATION (KCF) – EASTERN ENGLAND

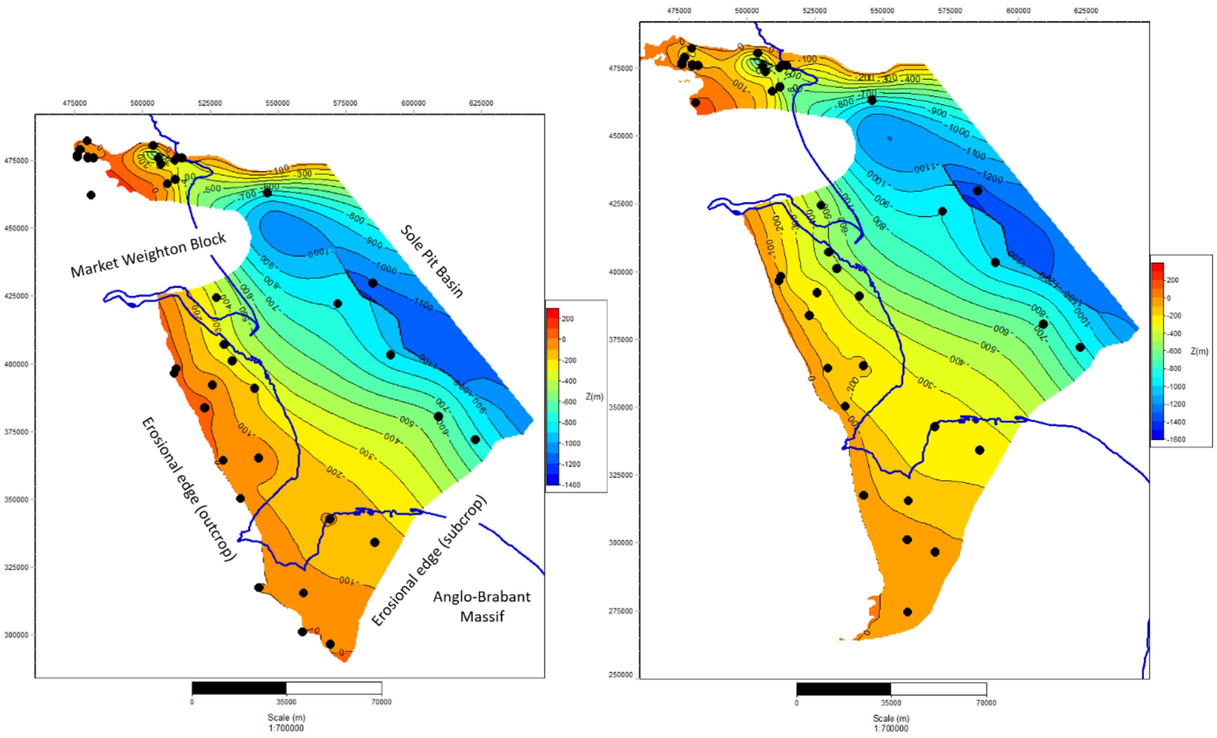


Figure 18. Top and base of Kimmeridge Clay Formation (KCF) in eastern England and offshore.

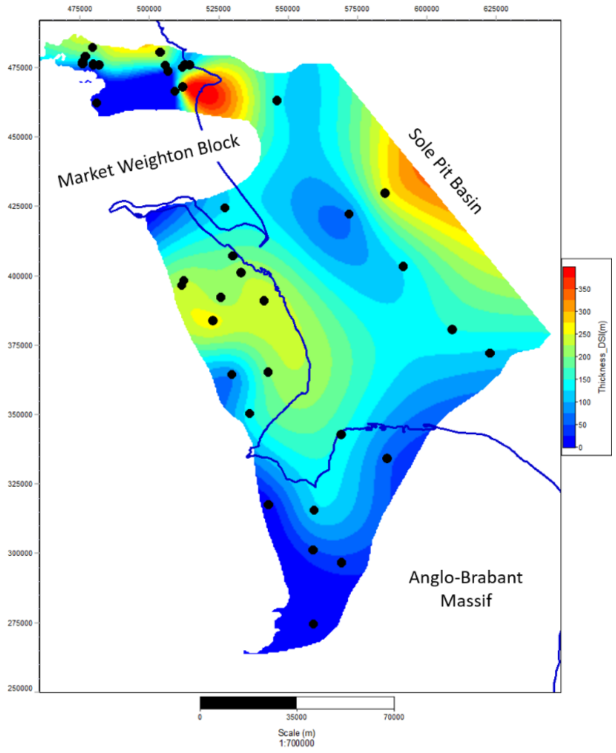


Figure 19. Preserved thickness of the Kimmeridge Clay Formation (KCF), eastern England.

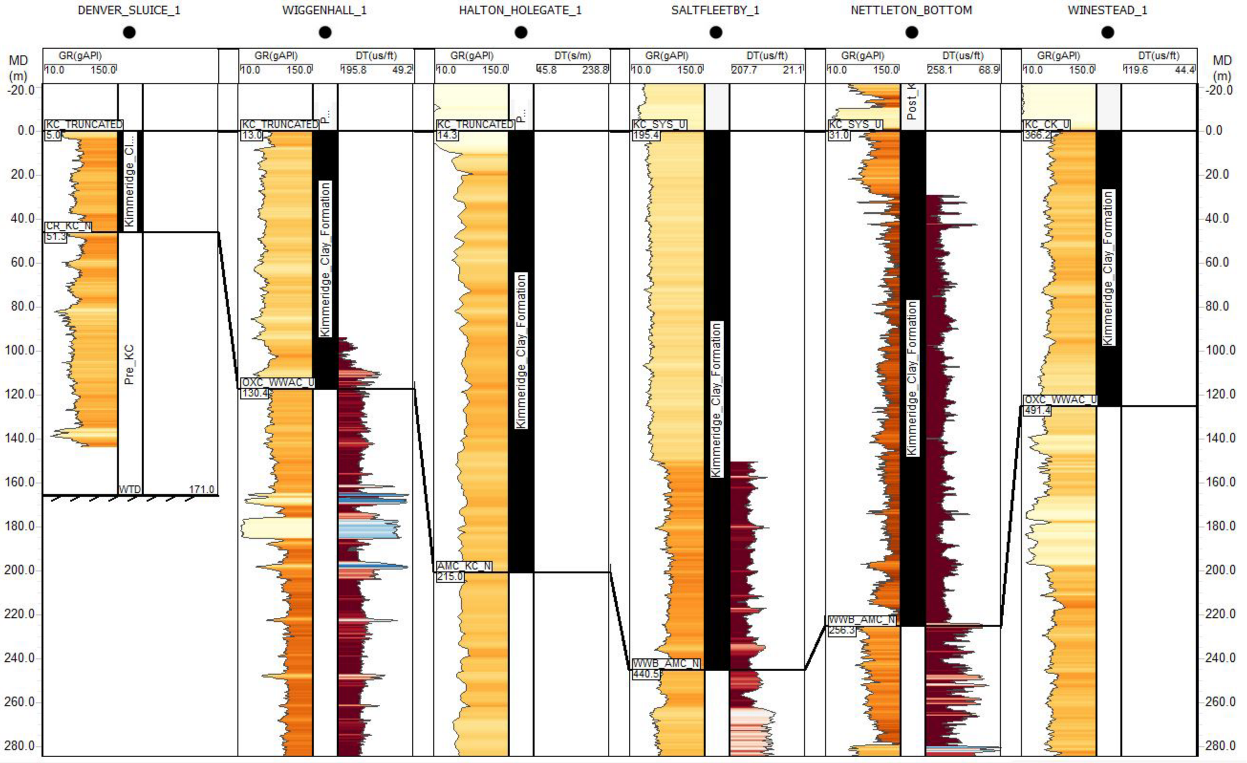


Figure 20. Lithological sections across eastern England (Denver Sluice to Winestead) showing Kimmeridge Clay Formation (KCF) thickness; MD: measured depth (m). Contains British Geological Survey materials © UKRI (2022).

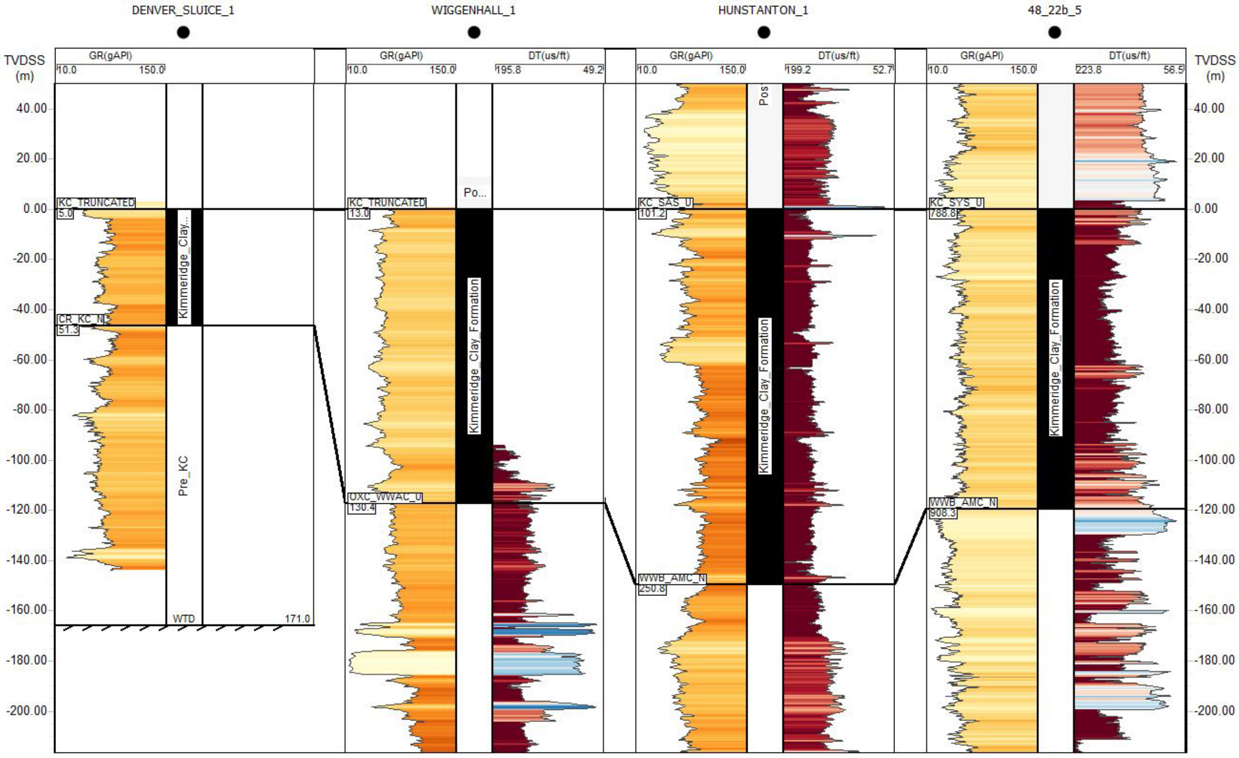


Figure 21. Lithological sections across eastern England and offshore (Denver Sluice to 48_22b_S); TVDSS: true vertical depth sub-sea level. Contains British Geological Survey materials © UKRI (2022).

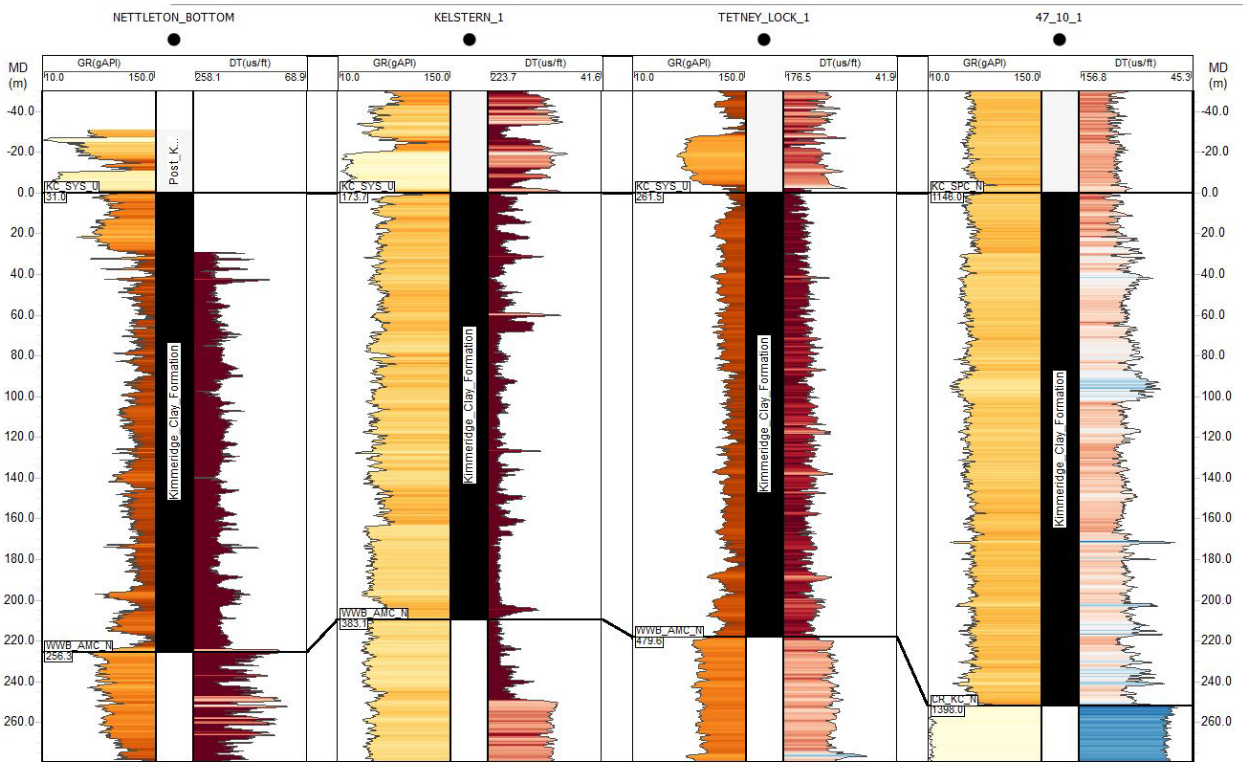
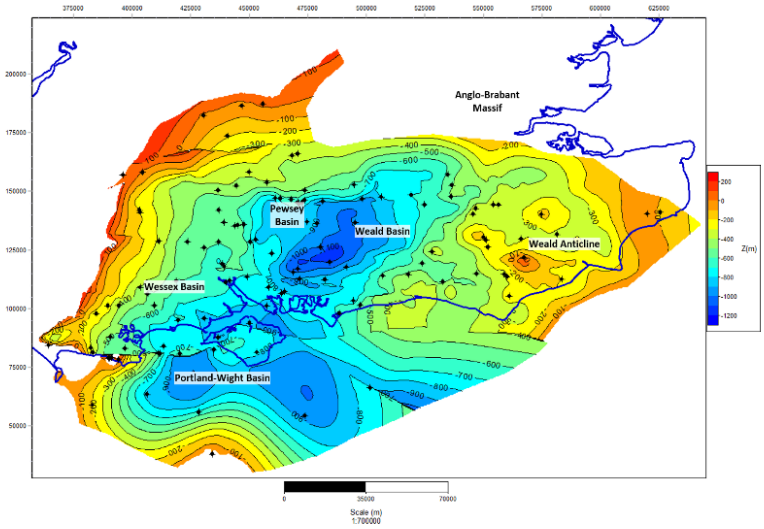


Figure 22. Lithological sections across eastern England (Nettleton Bottom to 47_10_1). Section is flattened on top of Kimmeridge Clay Formation (KCF) and boreholes are not at true relative elevation; MD: measured depth (m). Contains British Geological Survey materials © UKRI (2022).

KIMMERIDGE CLAY FORMATION (KCF) – WESSEX BASIN



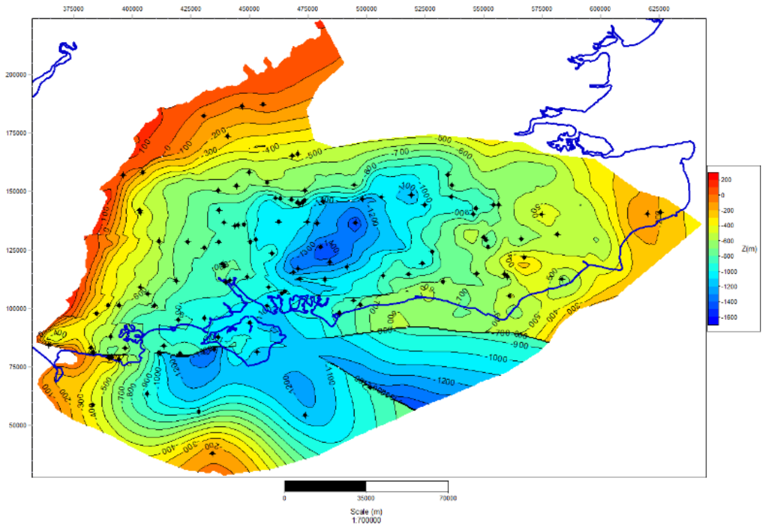


Figure 23. Top and base of the Kimmeridge Clay Formation (KCF) in the Wessex Basin and offshore.

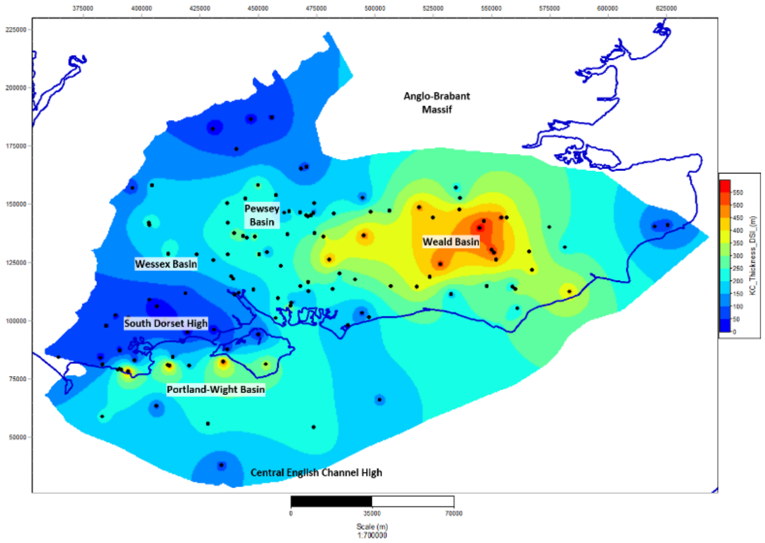


Figure 24. Preserved thickness of the Kimmeridge Clay Formation (KCF), Wessex Basin other basins in southern England, including offshore.

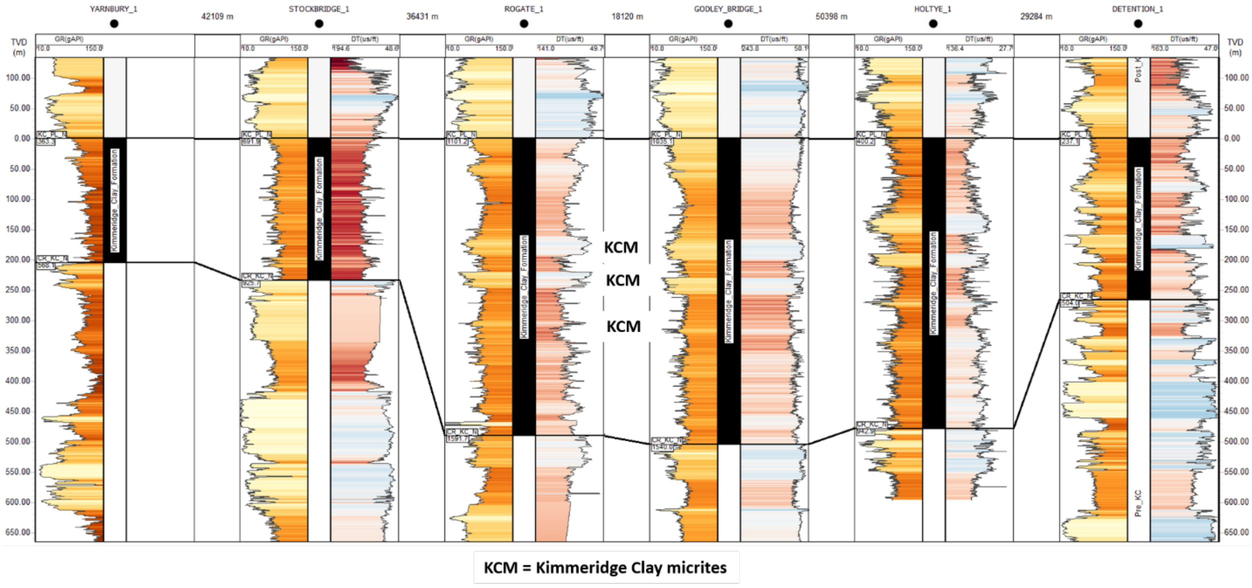


Figure 25. West to east lithological sections of the Kimmeridge Clay Formation (KCF), Wessex Basin showing thickness of unit. Section is flattened on top of KCF and boreholes are not at true relative elevation. TVD: true vertical depth (m). Contains British Geological Survey materials © UKRI (2022).

OXFORD CLAY FORMATION (OCF)

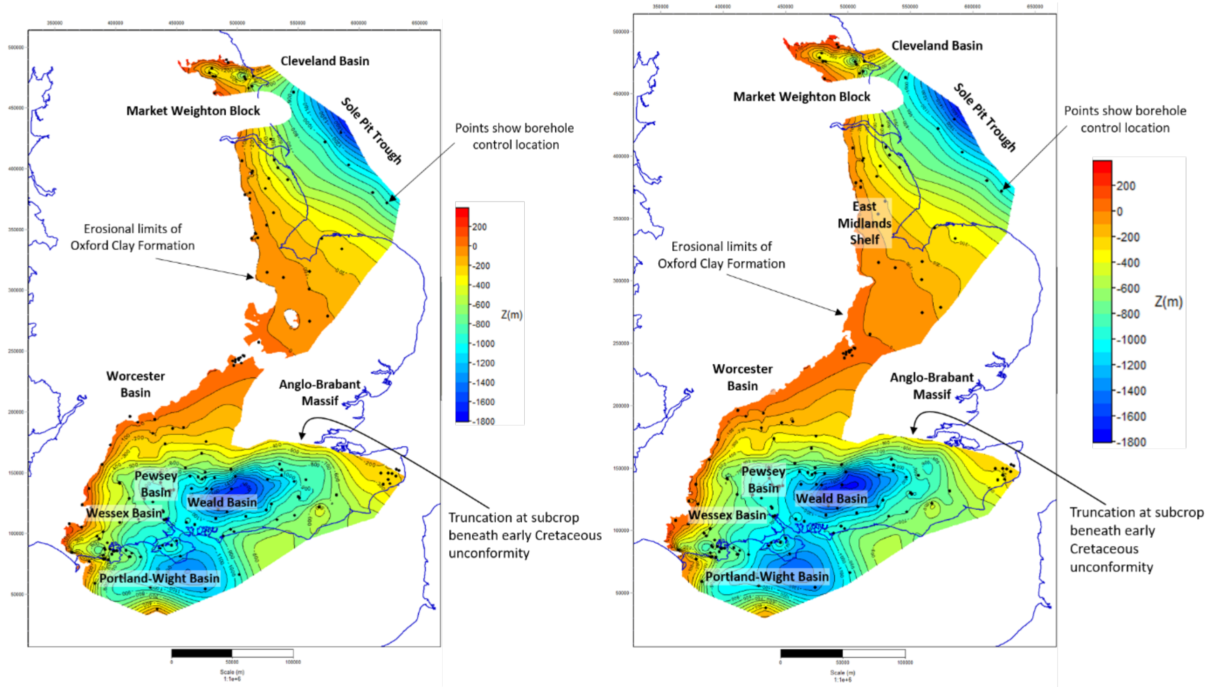


Figure 26. Top and base of the Oxford Clay Formation (OCF) in east and southern England.

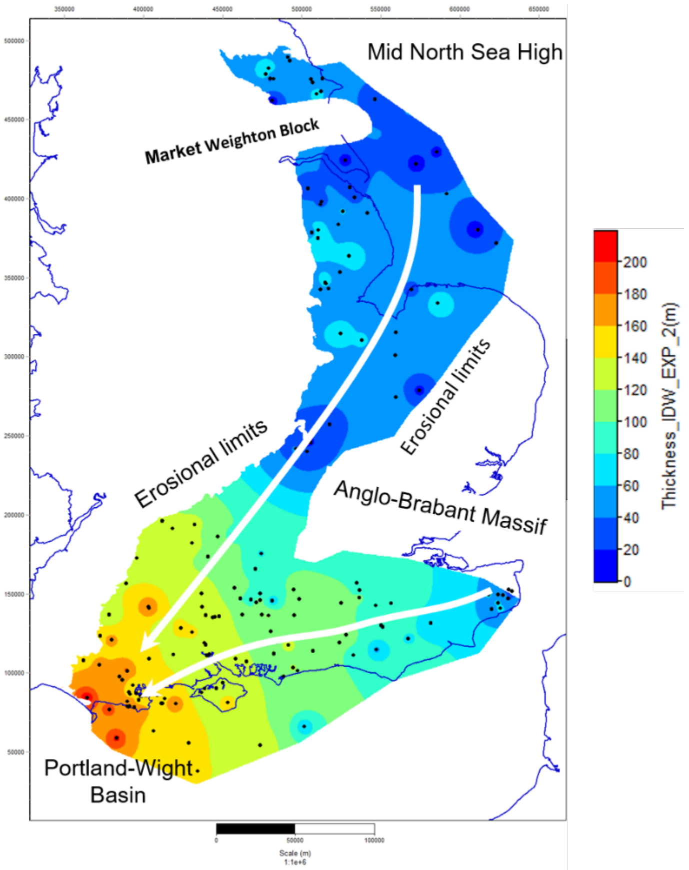


Figure 27. Preserved thickness of the Oxford Clay Formation (OCF); white arrows show thickening trend.

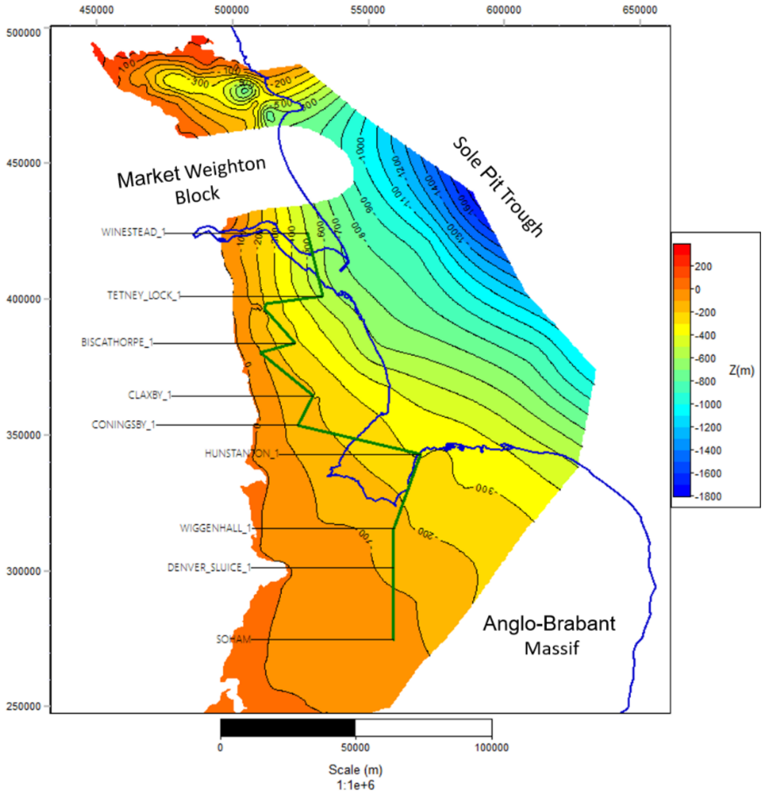


Figure 28. Structure section for the Oxford Clay Formation (OCF), eastern England.

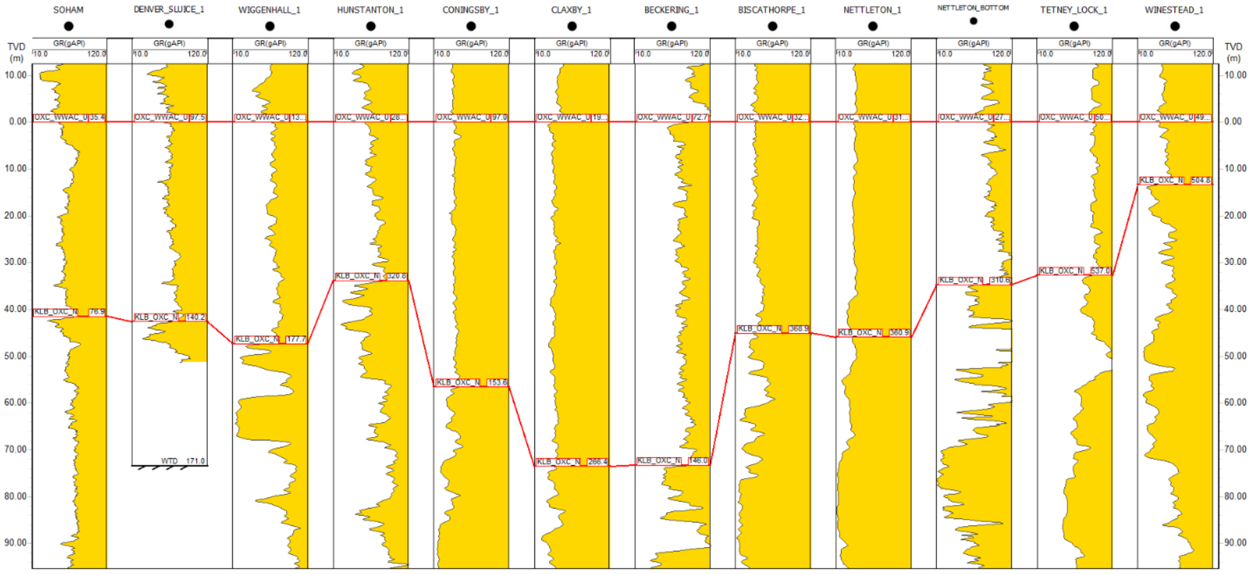


Figure 29. Correlation of lithological logs showing the spatial variation in thickness of the Oxford Clay Formation (OCF), eastern England (line of section given in Figure 28); TVD: true vertical depth (m). Contains British Geological Survey materials © UKRI (2022).

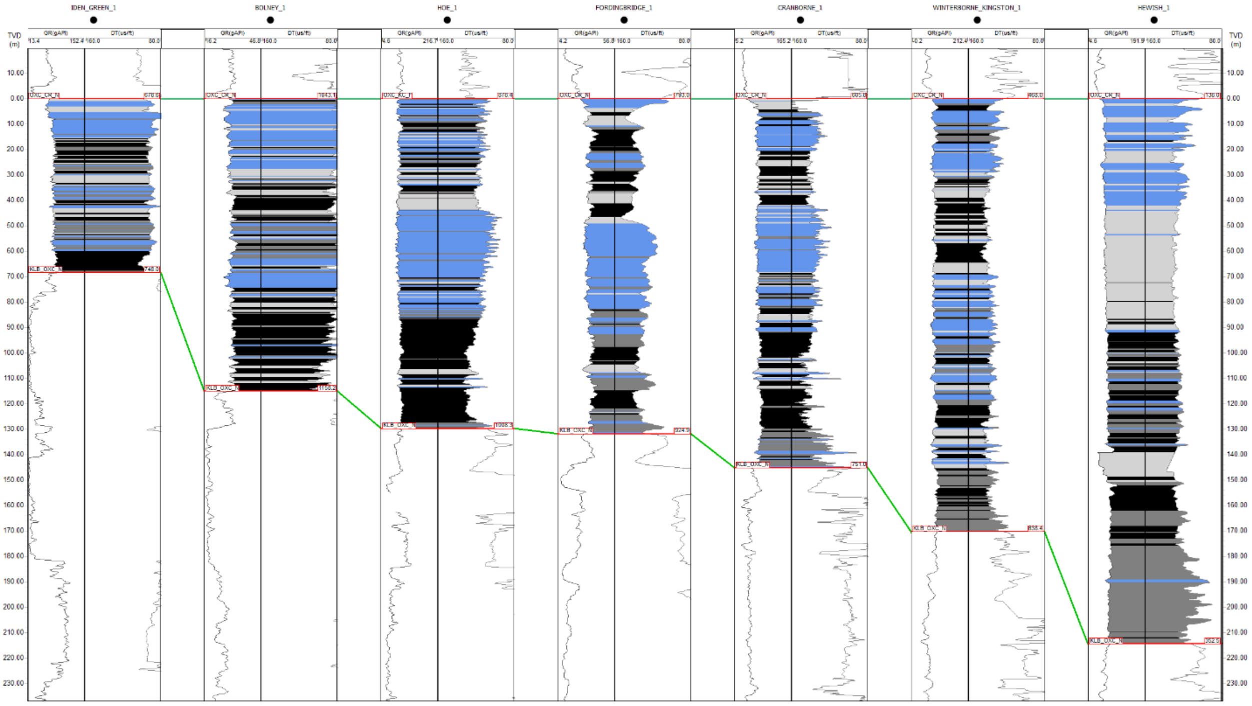


Figure 30. Correlation of lithological logs for the Oxford Clay Formation (OCF) showing thickness variation, Wessex Basin; TVD: true vertical depth (m). Contains British Geological Survey materials © UKRI (2022).

MERCIA MUDSTONE GROUP (MMG)

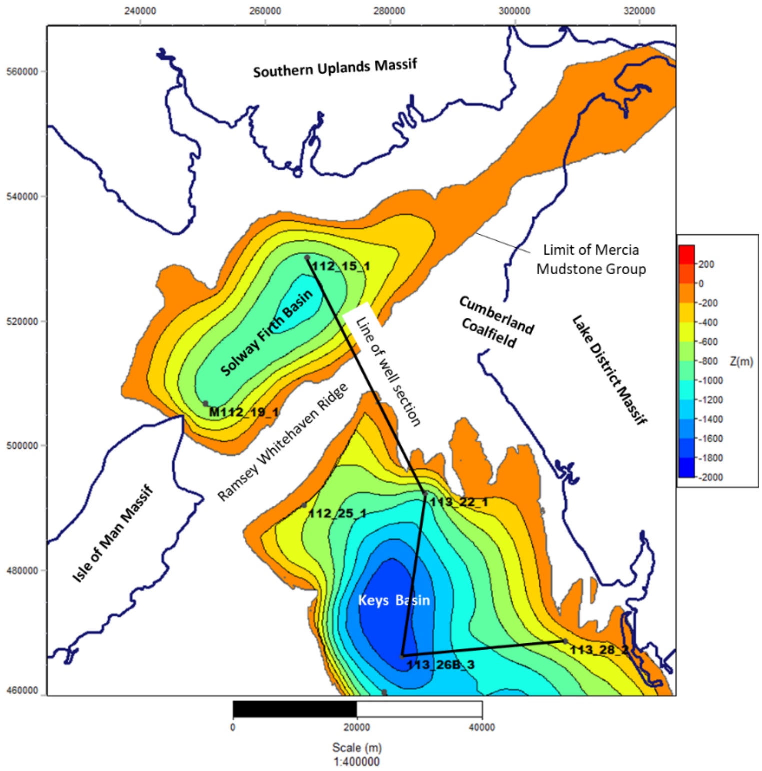


Figure 31. Elevation of the base of the Mercia Mudstone Group (MMG), East Irish Sea Basin (faults not shown).

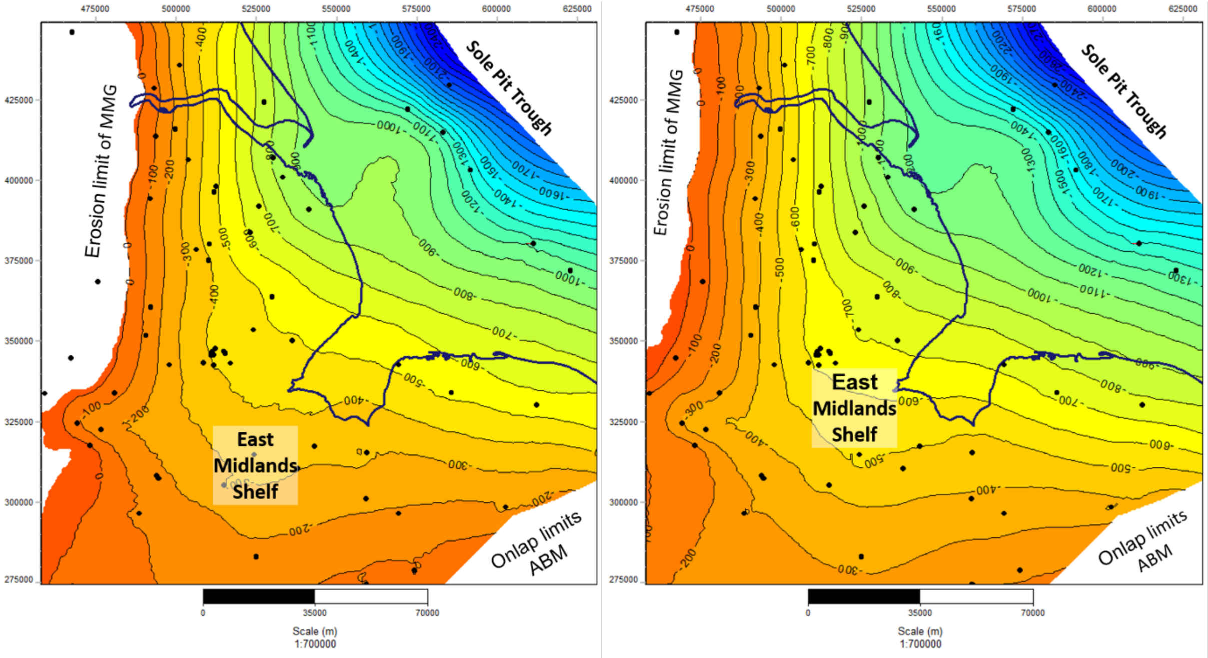


Figure 32. Elevation of the top and base of the Mercia Mudstone Group (MMG), eastern England and offshore.

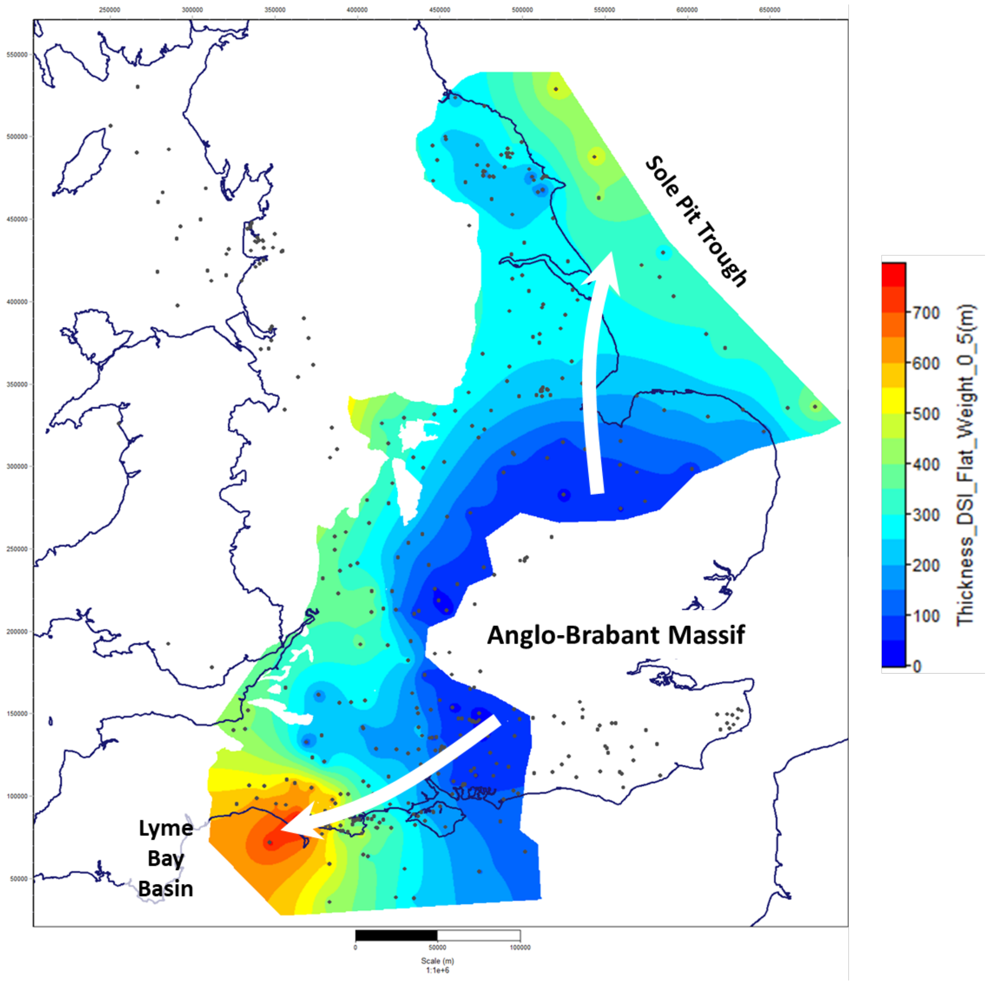


Figure 33. Preserved thickness of the Mercia Mudstone Group (MMG), east, north-east and southern England; white arrows show thickening trend.

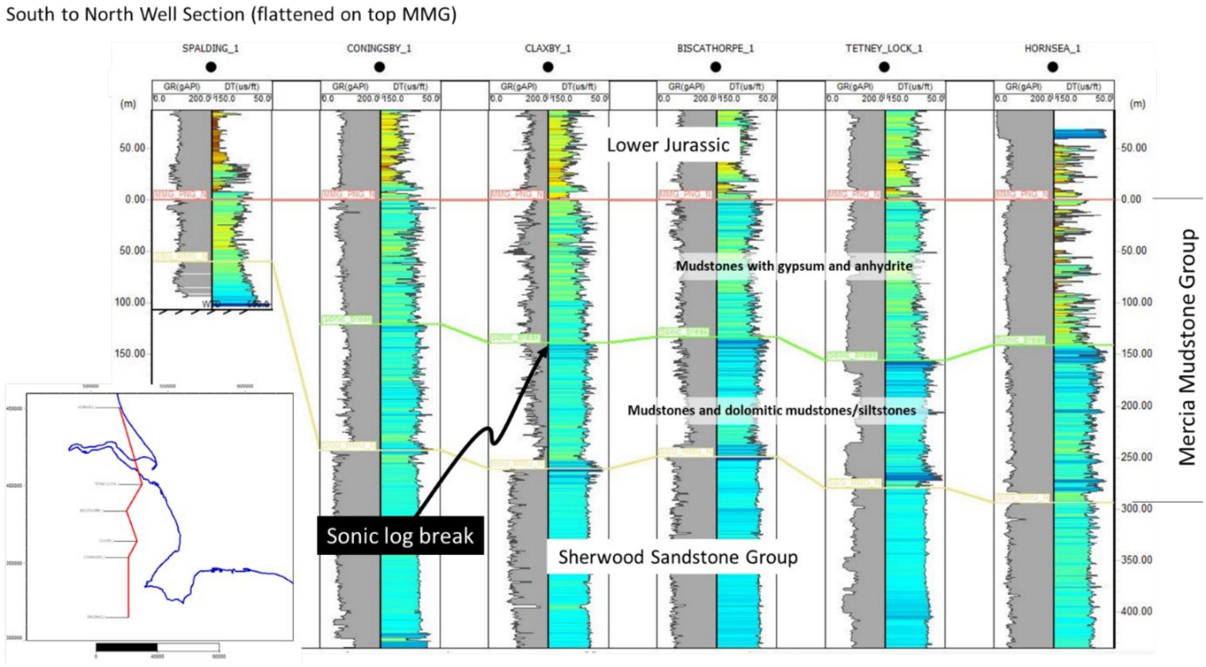


Figure 34. Lithological sections of the Mercia Mudstone Group (MMG) from Spalding to Hornsea, eastern England. Contains British Geological Survey materials © UKRI (2022).

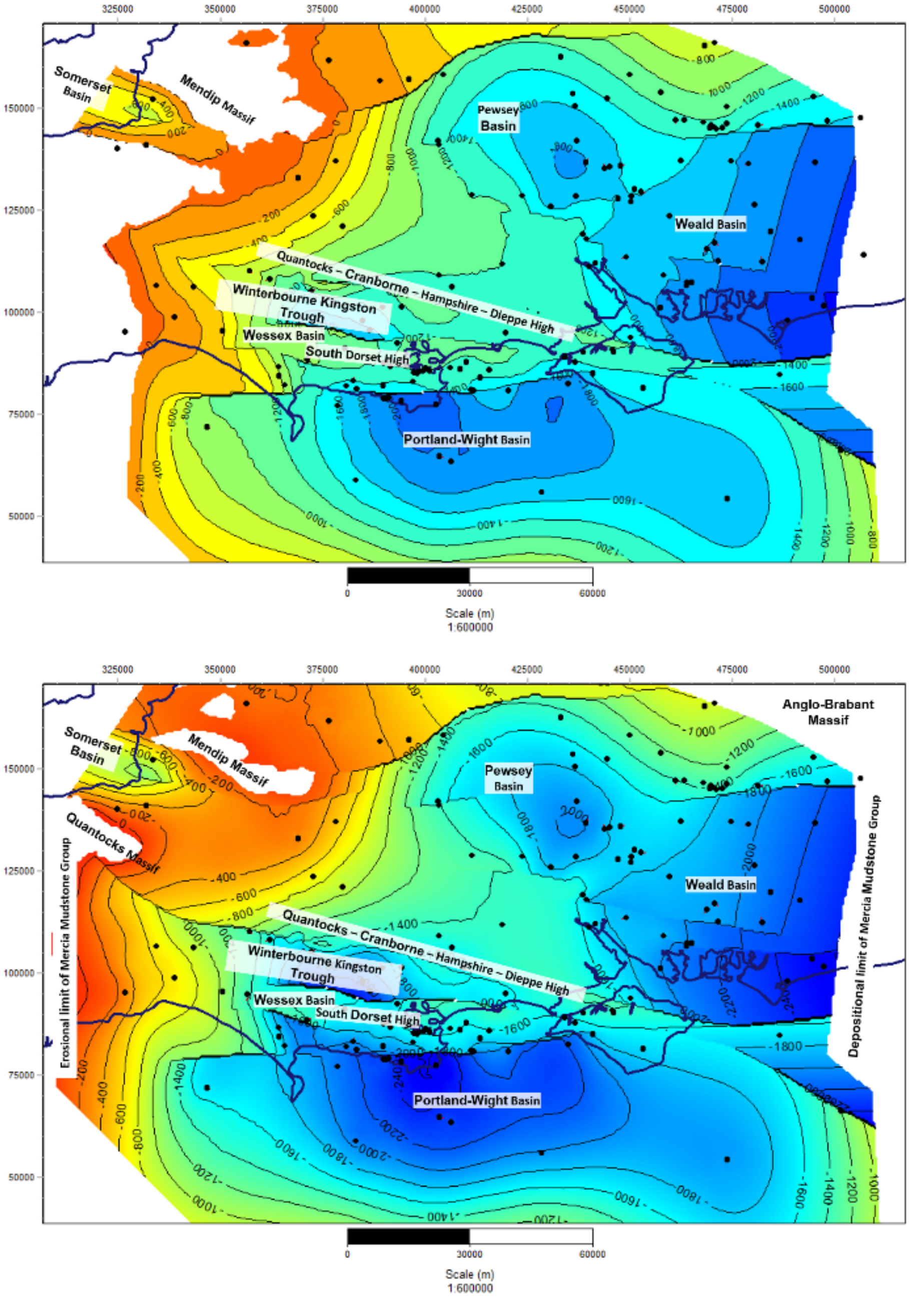


Figure 35. Elevation of the top and base of the Mercia Mudstone Group (MMG), Wessex Basin, southern England including offshore.

MERCIA MUDSTONE (MMG) HALITE DEPOSITS

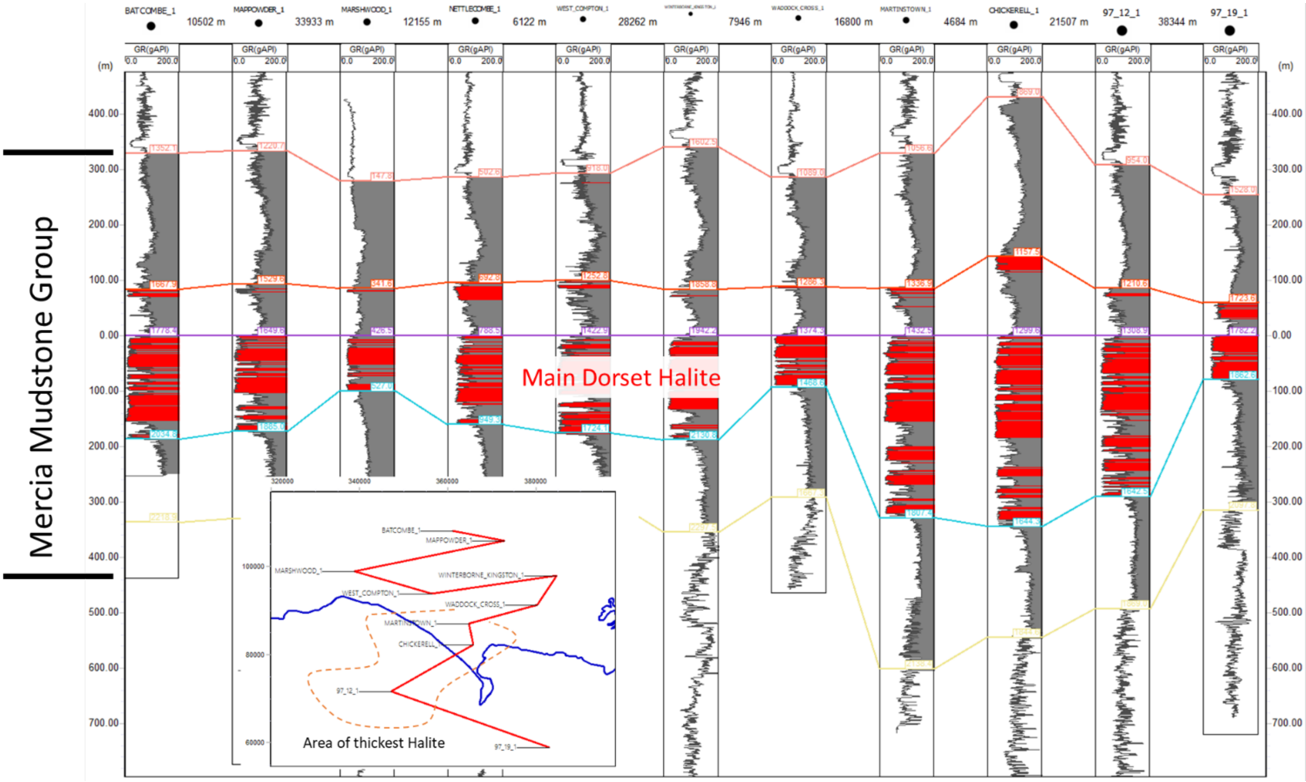


Figure 36. Lithological sections of the Dorset Halite, southern England. Contains British Geological Survey materials © UKRI (2022).

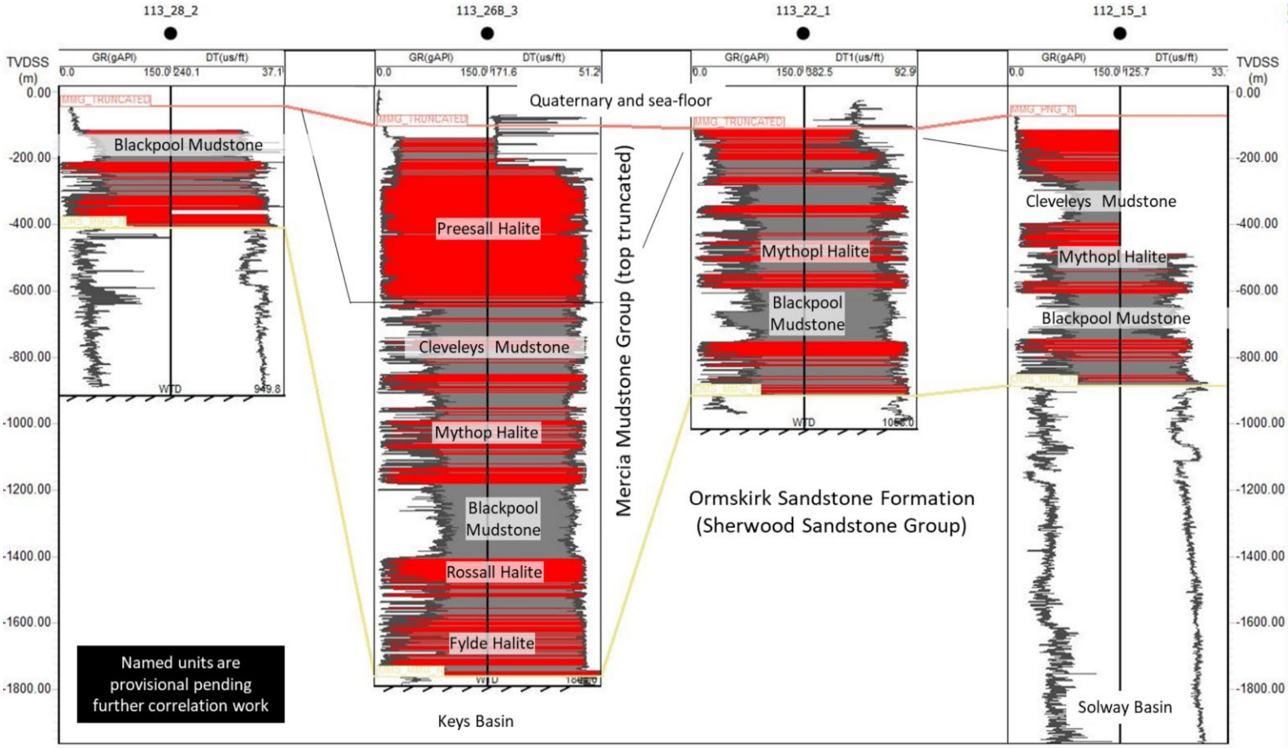


Figure 37. Lithological sections of the Irish Sea Halite ; TVDSS: true vertical depth sub-sea level. Contains British Geological Survey materials © UKRI (2022).

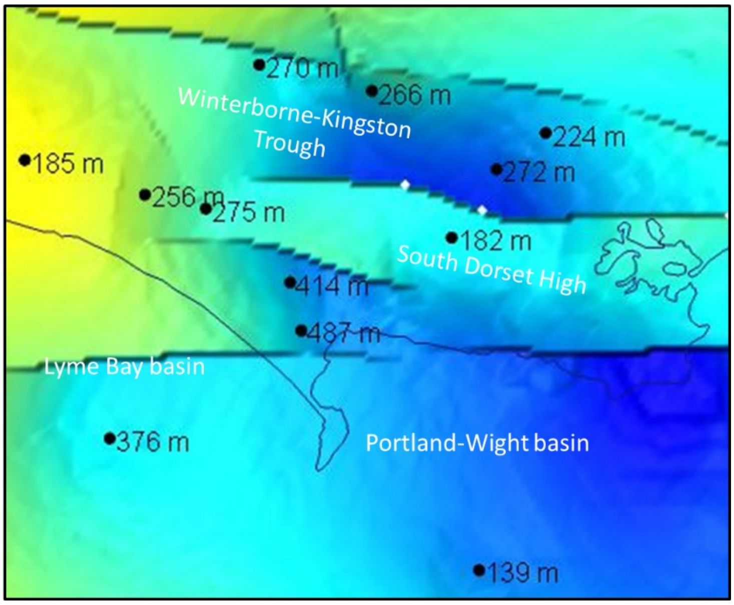


Figure 38. Preserved thickness of halite-bearing interval, Dorset Halite (contains interbedded mudstones), southern England.

Appendix 3 Summary groundwater/porewater data

METADATA AND MAJOR IONS

Source sample name	Location	County	Rock type	Sample type	Depth sample	Depth borehole	Data source	pH	Cond at 20°C (µS/cm)	Cond at 25°C (µS/cm)	Cond unknown (µS/cm)	Temp (°C)	TDS (mg/L)	DO (%)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)
Confidence in data																					
High																					
Moderately high																					
Moderate																					
Moderately low																					
Low																					
HW3/38	Harwell	Oxon	KC	PW	163		Brightman et al. 1985	6.6					6645		42.0	10.94	2561	16.8	3438	571	10.4
HW4/94	Harwell	Oxon	KC	PW	179		Brightman et al. 1985	4.8					15978		500	125	4582	54.3	3606	7108	2.44
13994-0002	Pickering	North Yorks	KC	PW	27		BGS data						6151		188	56.5	1591	13.2	490	3389	411
13994-0003	Pickering	North Yorks	KC	PW	42		BGS data						15063		265	84.1	4312	20.2	236	9614	532
13994-0004	Pickering	North Yorks	KC	PW	61		BGS data						10568		84.5	35.3	3012	11.3	227	6262	937
Ashdown No 1	Crowborough	East Sussex	KC	GW	629	1383	Wellmaster	7.4					35692		404	12	13509	23	20585	781	770
Ashdown No 1	Crowborough	East Sussex	KC	GW	702	1383	Wellmaster	7.8					22164		200	12	8822	34	13000	592	1010
Salton Manor	Pickering	North Yorks	KC	GW		91.6	Wellmaster						400		25.6	0.86	129		85.9	14.5	257
Steeple Ashton	Steeple Ashton	Wilts	KC	GW		38.4	Wellmaster						5242						2747		
M2/	Milton	Oxon	KC	PW	34		Brightman et al. 1985	8.6					3537		24.2	14.8	1352	13.7	1656	312	336
M2/2	Milton	Oxon	KC	PW	49		Brightman et al. 1985	8.5					3337		17.6	13.3	1271	9.0	1727	86	433
M2/4	Milton	Oxon	KC	PW	49		Brightman et al. 1985	8.8					3441		21.4	12.5	1271	11.3	1812	58	519
M2/3	Milton	Oxon	KC	PW	54		Brightman et al. 1985	8.6					3626		22.4	14.6	1354	14.9	1918	53	506
M2/5	Milton	Oxon	KC	PW	54		Brightman et al. 1985	7.4					9303		179	59.3	2409	49.7	3070	3403	268
MF2/2	Marcham	Oxon	KC	PW	6.7		Brightman et al. 1985	7.6					569		24.2	7.3	239	5.5	216	76.8	

Source sample name	Location	County	Rock type	Sample type	Depth sample	Depth borehole	Data source	pH	Cond at 20°C (µS/cm)	Cond at 25°C (µS/cm)	Cond unknown (µS/cm)	Temp (°C)	TDS (mg/L)	DO (%)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)
MF2/7	Marcham	Oxon	KC	PW	13		Brightman et al. 1985						1377		15.8	7.8	503	4.3	730	115	
HW4/115	Harwell	Oxon	OC	PW	224		Brightman et al. 1985						27780		673.1	301.3	5979	62.9	5250	15513	
HW4/141	Harwell	Oxon	OC	PW	250		Brightman et al. 1985	5					38322		300.1	58.3	6851	126	9498	21488	1.2
HW4/155	Harwell	Oxon	OC	PW	260		Brightman et al. 1985	6.2					23081		507.7	268.9	5793	95.4	5054	11335	54.9
HW4/172	Harwell	Oxon	OC	PW	283		Brightman et al. 1985	3.9					16083		150.0	9.7	5012	53.6	3634	7223	1.2
HW4/185	Harwell	Oxon	OC	PW	292		Brightman et al. 1985	8					12700		300.1	143.2	4097	21.1	4151	3813	354
HW4/202	Harwell	Oxon	OC	PW	318		Brightman et al. 1985	4.9					39306		274.1	71.7	5414	81.3	5422	28039	8.5
DA1/5.50-5.70	Down Ampney	Gloucs	OC	PW	5.6		Metcalfe et al. 1990	8.1					569		26.5	4.69	185	2.95	141	23	377
DA1/9.3-9.7	Down Ampney	Gloucs	OC	PW	9.5		Metcalfe et al. 1990	8.3					935		7.4	3.03	343	3.44	320	64	394
DA1/14.00-14.4	Down Ampney	Gloucs	OC	PW	14.2		Metcalfe et al. 1990	7.6					5127		122	76.3	1510	9.12	441	2850	242
DA1/18.48-18.88	Down Ampney	Gloucs	OC	PW	18.7		Metcalfe et al. 1990	8.5					2011		5.4	3.50	702	3.45	581	454	532
DA2/11.71-12.11	Down Ampney	Gloucs	OC	PW	11.9		Metcalfe et al. 1990	8.2					1656		16.7	9.14	634	5.41	700	112	363
DA2/20.70-21.10	Down Ampney	Gloucs	OC	PW	20.9		Metcalfe et al. 1990	8.4					2642		9.3	6.63	1070	5.54	1210	106	476
DA2/33.05-33.45	Down Ampney	Gloucs	OC	PW	33.2		Metcalfe et al. 1990	8.5					3104		8.4	6.45	1250	4.60	1550	50	477
DA2/44.39-44.78	Down Ampney	Gloucs	OC	PW	44.6		Metcalfe et al. 1990	7.3					10477		208	114	3620	19.70	1670	4620	458
DA2/54.50-54.90	Down Ampney	Gloucs	OC	PW	54.7		Metcalfe et al. 1990	8.2					5035		27.0	16.4	1870	6.97	2600	349	337
DA2/63.39-63.79	Down Ampney	Gloucs	OC	PW	63.6		Metcalfe et al. 1990	8.7					4663		19.6	13.2	1850	7.07	2370	213	386
DA/11/5.06-5.36	Down Ampney	Gloucs	OC	PW	5.2		Metcalfe et al. 1990	8.0					470		21.4	5.27	176	3.44	108	8	302
DA/11/15.7-16.2	Down Ampney	Gloucs	OC	PW	16		Metcalfe et al. 1990	8.7					1083		3.8	2.91	446	3.10	404	50	352
DA/11/25.5-26	Down Ampney	Gloucs	OC	PW	25.8		Metcalfe et al. 1990	8.8					1313		2.3	1.51	556	2.28	488	29	475
DA20/1	Down Ampney	Gloucs	OC	GW	15.2		Metcalfe et al. 1990	8.46					360		82.0	9.51	38.0	4.69	28	57	286
DA20/2	Down Ampney	Gloucs	OC	GW	15.2		Metcalfe et al. 1990	7.8			1710	21.9	988		36.4	6.21	360	7.89	264	66	504
DA13/2	Down Ampney	Gloucs	OC	GW	25		Metcalfe et al. 1990	7.6					498		169	5.57	28.9	10.60	40	66	360
DA13/3	Down Ampney	Gloucs	OC	GW	25		Metcalfe et al. 1990	8.38			3010	19.8	1682		24.9	3.55	666	11.40	491	127	728
Norwest Holst Soil	Elstow	Beds	OC	GW			Ross et al. 1989	7.01					3358		340	156	508	33.70	650	1430	488

Source sample name	Location	County	Rock type	Sample type	Depth sample	Depth borehole	Data source	pH	Cond at 20°C (µS/cm)	Cond at 25°C (µS/cm)	Cond unknown (µS/cm)	Temp (°C)	TDS (mg/L)	DO (%)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)
Engineering. Groundwater median values Elstow BB1 and BB2	Elstow	Beds	OC	PW	19		Ross et al. 1989	7.9					1963		169	368	313	8.64	59	930	234
Didcot	Didcot	Oxon	OC	GW		105	Burley et al 1984						10724		283	205	2861		5720	1595	122
OBH(P) WRB NO. SD43/207/1.1/11	Kirkham	Lancs	MMG	GW		445	Wilson et al. 2019	7.4	251500				136487		1285	503	51550	61	77000	6085.0	3.1
Kirkham	Kirkham	Lancs	MMG	GW	350		BGS data						170336		1476	562	66242	58	95176	6822	<5
EA Observation borehole near Kirkham	Kirkham	Lancs	MMG	GW	240	445	Arup 2014	7.23	204000			11.3	154437	11.4	1150	420	55800	67.10	91000	6000	<6.1
EA Observation borehole near Kirkham	Kirkham	Lancs	MMG	GW	260	445	Arup 2014	7.5	299000			12.3	119780	6.1	1350	497	48700	63.30	63000	6170	<6.1
M1	Retford	Notts	MMG	GW		Shallow	Smedley et al. 2018	7.03		2450			2170		579	74.1	33.1	5.60	41.6	1250	380
M2	Retford	Notts	MMG	GW		Shallow	Smedley et al. 2018	7.70		966			450		64.6	48.4	24.9	6.20	55.2	158	188
M3	Retford	Notts	MMG	GW		Shallow	Smedley et al. 2018	7.52		1185			648		95.4	46.8	29	72.30	70.8	104	467
M4	New Ollerton	Notts	MMG	GW		Shallow	Smedley et al. 2018	7.18		603			349		61.6	30.3	11.7	24.30	26.8	81	230
M5	Retford	Notts	MMG	GW		4.1	Smedley et al. 2018	7.3		589			351		63	24.3	18.8	23.30	23.4	75.3	249
M6	Retford	Notts	MMG	GW		3.7	Smedley et al. 2018	7.19		1770			1052		131	58.9	152	51.20	338	130	389
Stow on the Wold 1	Stow-on-the-Wold	Gloucs	MMG	GW	321	365	Burley et al. 1984	7.7					1474		122	20	337	3	148	822	44
Somerton 1	Somerton	Norfolk	MMG	GW	683	1397	Burley et al. 1984	7.1					52418		3000	800	16700	240	31000	580	200
Leicester 1	Leicester	Leics	MMG	GW	40		Cheney 2004						700								
Leicester 2	Leicester	Leics	MMG	GW	60		Cheney 2004						2600								
Leicester compiled	Leicester	Leics	MMG	GW			Cheney 2004						1662						80	711.5	1769
Agden Brine 70	Lymm	Cheshire	MMG evaporite	GW	70		Tellam 1995	7.0				22	8985		159	12	3350	10.00	5000	434	41
Agden Brine 120	Lymm	Cheshire	MMG evaporite	GW	120		Tellam 1995	6.8				22	15916		177	22	5950	13.00	9256	481	35
Agden Brine 150	Lymm	Cheshire	MMG evaporite	GW	150		Tellam 1995	5.75				22	321056		1224	411	122500	105.00	192060	4690	135

MINOR AND TRACE ELEMENTS

Source sample name	Br (mg/L)	DOC (mg/L)	F (mg/L)	NH_4 (mg/L)	NO_3 (mg/L)	SiO_2 (mg/L)	TIC (mg/L)	TOC (mg/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)	CH_4 (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (µg/L)	Sr (µg/L)
HW3/38										1330			189900	236		2720
HW4/94										1080			474700	951		22300
13994-0002	1.53		0.611		12.6	11.0	80.9		<2	3785	38.3		63		262	9416
13994-0003	0.906		0.126		<0.6	9.01	104.7		8	2979	66.0		45		257	13992
13994-0004	0.673		0.482		<0.6	8.09	184.4		23	2959	31.5		169		121	7194
Ashdown No 1																
Ashdown No 1																
Salton Manor					<DL								2691			
Steeple Ashton																
M2/													3348	243		1183
M2/2													1116	257		876.2
M2/4													837	229		920.0
M2/3													3906	242.9		1270
M2/5													151497	666		6922
MF2/2													3906	194		438.1
MF2/7													3348	229		1008
HW4/115						0.85				1080			94940	1500		29570
HW4/141						3.95				649			1499400	5000		9945
HW4/155						4.21				1480			178700	1055		17090
HW4/172						0.99				937			1195100	673		7010
HW4/185						0.99				1945			19550	569		10650
HW4/202						1.93				17700			968900	1120		9730
DA1/5.50-5.70	0.600		1.47	0.45	0.1	9.18	66.0	35	<50		20.0		<10		28.0	417
DA1/9.3-9.7	1.36		2.29	0.75	<0.25	6.08	72.0	46	<100		7.0		<20		16.0	312
DA1/14.00-14.4	<2.5		1.34	1.63	<2.5	6.95	40.0	31	<100		133		98		177	8390
DA1/18.48-18.88	3.52		2.89	0.87	<1	5.16	95.0	38	<100		17.0		<20		37.0	399
DA2/11.71-12.11	2.93		1.70	0.5	<0.5	6.42	62.0	51	<100		18.0		484		22.0	968
DA2/20.70-21.10	5.12		2.51	0.34	<1	5.82	88.0	47	<50		36.0		44		20.0	741

Source sample name	Br (mg/L)	DOC (mg/L)	F (mg/L)	NH_4 (mg/L)	NO_3 (mg/L)	SiO_2 (mg/L)	TIC (mg/L)	TOC (mg/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)	CH_4 (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (µg/L)	Sr (µg/L)
DA2/33.05-33.45	7.28		2.43	0.83	<1	4.73	90.0	44	<100		10.0		<20		4.0	728
DA2/44.39-44.78	6.10		0.98	2.23	<2.5	4.92	86.0	73	<100		112		213		343	16000
DA2/54.50-54.90	10.9		2.24	1.05	<2.5	3.53	64.0	52	<100		33.0		<20		24.0	2010
DA2/63.39-63.79	9.60		3.30	0.87	<2.5	4.62	71.0	45	<100		27.0		<20		18.0	1590
DA/11/5.06-5.36	0.52		4.51		0.34	5.67	60.8	30.8	<50		16.0		<10		13.0	507
DA/11/15.7-16.2	2.27		3.30		0.31	4.60	75.2	38.2	<100		3.0		<20		<3	310
DA/11/25.5-26	2.65				0.22	5.67	104.0	31.4	60		5.0		<10		4.0	161
DA20/1	0.11		0.61		0.19	8.58	54.6	45.8			29.0		<10		34.0	502
DA20/2	1.30		3.08	1.47	1.73	4.24	83.0	18.6		2610	70.0		39		15.0	670
DA13/2	0.12		0.17		121	3.64	68.4	72.2			50.0		<10		30.0	482
DA13/3	2.70		3.56	142	20.5	8.58	132.0	26		3310	70.0		20	50	4.0	700
Norwest Holst Soil Engineering. Groundwater median values				<0.5	0.7	8.16		33.5	240				70		170	
Elstow BB1 and BB2	<0.25		1.20		<0.5	9.54		21.3	<300		10.0		200		100	4020
Didcot						55.0										
OBH(P) WRB NO. SD43/20 7/1.1/11											112.0		46650		1034.0	19050
Kirkham			<5	0.98	<30	<7.3			305	1726	58	6.7	561	2456	232	21353
EA Observation borehole near Kirkham		1.08	0		<0.868	1.40			<100	1610	<100	<0.5	3340	2180	648	19200
EA Observation borehole near Kirkham		1.07	0		<0.868	0.93			<100	1240	<100	<0.5	1140	1790	198	17100
M1					17.2					240				77		5030
M2					52.7					120				18		106
M3					42.8					200				19		515
M4					39.4					79				<7		70
M5					22.1					200				20		250
M6					66.8					90				20		1040
Stow on the Wold 1																

Source sample name	Br (mg/L)	DOC (mg/L)	F (mg/L)	NH$_4$ (mg/L)	NO$_3$ (mg/L)	SiO$_2$ (mg/L)	TIC (mg/L)	TOC (mg/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)	CH$_4$ (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (µg/L)	Sr (µg/L)
Somerton 1																
Leicester 1																
Leicester 2																
Leicester compiled																
Agden Brine 70	4		0.26	<0.06	3.84	1				300			29000		<10	4900
Agden Brine 120	12		0.31	<0.06	2.13	0.6				450			12000		<10	3600
Agden Brine 150	112		0.33	<0.06	0.04	1.5				2500			25000		<10	30000

Confidence in data

high

moderately high

moderate

moderately low

low

Appendix 4 PHREEQC model inputs

The following tables provide a summary of the models developed to derive credible reference water compositions for the areas of interest. The numbers provided in the tables refer to the corresponding numbers of the input files related to each model (see the remainder of the appendix), while the information provided in the brackets refers to the reference waters (RW) obtained from those models. EM stands for “End Member”, while BW stands for “Boundary Water”.

The models have been developed using the widely used, public-domain PHREEQC v 3.7.1.15876 software (Parkhurst and Appelo, 2013). This software was used together with thermodynamic databases Thermochimie v 10a (Giffaut et al., 2014) and THEREDA 2020 release (Moog et al., 2015). The first of these thermodynamic databases is used for Jurassic clays (OCF and KCF), whereas the latter is used for halite-bearing sequences (MMG).

East Irish Sea Basin

	EM1 (Sellafield BH3, concentrated)	EM2 (Agden Brine)
No Mixing Model	1 (RW13)	2 (RW14)
BW1 (Sellafield freshwater BH2, Sherwood Sandstone Aquifer)	5 (RW1 – 3)	3 (RW7 – 9)
BW2 (Standard Seawater)	6 (RW4 – 6)	4 (RW10 – 12)

East Lincolnshire

	EM1 (Sellafield BH3, concentrated)	EM2 (Agden Brine)	EM3 (Standard Seawater in equilibrium with KCF rock minerals)	EM4 (Standard Seawater in equilibrium with OCF rock minerals)
No Mixing Model			9 (RW21)	11 (RW25)
BW3 (Welton location, Sherwood Sandstone Aquifer)	8 (RW15 – 17)	7 (RW18 – 20)		
BW4 (Spilsby Sandstone Aquifer)			10 (RW22 – 24)	
BW5 (BW4:EM3=1:1)				12 (RW26 – 28)

East Anglia

	EM5 (MMG water in equilibrium with MMG rock minerals)
No Mixing Model	13 (RW29)

Wessex Basin

	EM6 (Ashdown KCF water from 629 m in equilibrium with KCF rock minerals)	Ashdown KCF water from 702 m in equilibrium with KCF rock minerals	EM7 (Didcot OCF water in equilibrium with OCF rock minerals)
No Mixing Model	14a (RW30)	14b (RW31)	15 (RW32)

EAST IRISH SEA BASIN

1. Concentration of deep groundwater pumped from the Sherwood Sandstone Group at a depth of 1100 m in Sellafield borehole BH3 (Table 18) until the water becomes saturated with common evaporite minerals. The composition of water equilibrated with these minerals is taken as an estimate of groundwater in evaporite-bearing MMG. This approach is consistent with the interpreted origin of salinity in the sampled water from BH3 in the MMG of the East Irish Sea Basin (Bath et al., 2006).

```
SOLUTION 1      # Sellafield BH3 GW-DET1, Bath et al., 2006
temp       25
pH         7.0
units      mg/l
density    1.119
Na         71600
K          327
Ca         2520
Mg         686
Al         0.001 Gibbsite
Si         0.001 SiO2:2H2O(am)
Cl         108000 charge
S(6)       1637 as S
C(4)       10.82 as C

-water     1 # kg

SAVE SOLUTION 1

REACTION 1
H2O 1
-50 moles in 100 steps #1 kg of water is 55.51 moles, 5.551 moles H2O
removed per step (=100 ml H2O per step)
Incremental_Reactions True

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Halite 0   0
Anhydrite  0  0
Calcite 0  0
Dolomite 0 0

SAVE SOLUTION 2

SELECTED_OUTPUT
-file Calc1-Sellafield BH3 evaporation.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl S(6)  C(4)
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-saturation_indices Halite Anhydrite Calcite Dolomite
-equilibrium_phases Halite Anhydrite Calcite Dolomite
END
```

2. A reported composition of Agden Brine (Tellam, 1995), pumped from the MMG at a depth of 150 m in the Mersey Basin (Table 17) was modelled to assess whether it is saturated / over-saturated / undersaturated with halite.

```
SOLUTION 1      # Agden Brine BH3, Tellam, 1995
temp       25
pH         5.75
units      mg/l
density    1.201
Na         122500
K          105
Ca         1224
Mg         411
Al         0.001 Gibbsite
Si         0.7 SiO2:2H2O(am)
Cl         192100 charge
S(6)       1563 as S
C(4)       26.56 as C

-water     1 # kg

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc2-Agden Brine sat check.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg  Al  Mn Si Cl   S(6)  C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2

END
```

3. The composition of groundwater pumped from the Sherwood Sandstone Group at a depth of 206 m in Sellafield borehole BH2 (Bath et al., 2006) was treated as a typical freshwater from the Sherwood Sandstone aquifer (Table 18). A similar water could plausibly enter the MMG and mix with more saline in-situ water, here represented by Agden Brine (Tellam, 1995).

```
SOLUTION 1      # Boundary Water - Shallow aquifer fresh water DET 1A, Bath
et al., 2006
temp      25
pH        7.5
units     mg/l
density   0.9961
Na        13
K         2
Ca        33 Charge
Mg        11
Al        0.001 Gibbsite
Si        0.001 SiO2:2H2O(am)
Cl        12
S(6)      3 as S
C(4)      24.39 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc3-Sherwood&Agen mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl   S(6)  C(4)
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END

SOLUTION 2    # LSSR In situ water - Agden Brine Tellam, 1995
temp      25
pH        5.75
units     mg/l
density   1.199
Na        122261
K         104.8
Ca        1222
Mg        410.2
Al        23.59 Gibbsite
Si        14.65 SiO2:2H2O(am)
```

```
Cl        188572 charge
S(6)      1560 as S
C(4)      26.51 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2
END

MIX 1
1 0.001
2 0.999

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

```
MIX 5
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 10
```

```
1   0.99
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000
END
```

4. The composition of standard seawater (Millero et al., 2008) was considered as another potential water type that could penetrate the MMG and mix with more saline in-situ water represented by the Agden brine composition (Tellam, 1995).

```
SOLUTION 1      # Boundary Water - marine water, Millero et al., 2008
temp       25
pH         8.1
units      mg/L
density    1.02
Na         10995.7
K          407
Ca         420.3
Mg         1309
Al         0.001 Gibbsite
Si         0.001 SiO2:2H2O(am)
Cl         19737.3 charge
S(6)       923.2 as S
C(4)       21.04 as C

-water     1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc4-Seawater&Agden mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl   S(6)  C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END

SOLUTION 2    # LSSR In situ water - Agden Brine Tellam, 1995 (result of
Simulation #2)
temp       25
pH         5.75
units      mg/l
density    1.199
Na         122261
K          104.8
Ca         1222
Mg         410.2
Al         23.59 Gibbsite
Si         14.65 SiO2:2H2O(am)
Cl         188572 charge
S(6)       1560 as S
```

```
C(4)      26.51 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2

END

MIX 1
1 0.001
2 0.999

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 5
```

```
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 10
1   0.99
```

```
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

5. The composition of groundwater pumped from the Sherwood Sandstone Group at a depth of 206 m in Sellafield borehole BH2 (Bath et al., 2006) (Table 18) was considered as one potential water type that could be penetrating the MMG and mixing with more saline in-situ water (halite-saturated water derived by concentrating the Sherwood Sandstone Group water from Sellafield BH3 DET 1, (Bath et al., 2006) (see above).

```
SOLUTION 1      # Boundary Water - Shallow aquifer fresh water DET 1A, Bath
et al., 2006
temp       25
pH         7.5
units      mg/l
density    0.9961
Na         13
K          2
Ca         33 Charge
Mg         11
Al         0.001 Gibbsite
Si         0.001 SiO2:2H2O(am)
Cl         12
S(6)       3 as S
C(4)       24.39 as C

-water     1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc5-Sherwood&SellBH3 mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl   S(6)  C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END

SOLUTION 2    # LSSR In situ water - halite saturated water obtained by
concentrating the Sherwood Sandstone Group water from Sellafield BH3 DET 1,
Bath et al., 2006
temp       25
pH         5.94
units      mg/l
density    1.2
Na         121193
K          560.8
Ca         1797
```

```
Mg        1174
Al        0.01171 Gibbsite
Si        44.27 SiO2:2H2O(am)
Cl        192216 charge
S(6)      790.4 as S
C(4)      15.94 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2

END

MIX 1
1 0.001
2 0.999

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
```

```
SiO2:2H2O(am) 0 1000

END

MIX 5
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000
```

```
END

MIX 10
1   0.99
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

6. The composition of standard seawater (Millero et al., 2008) was considered as another potential water type that could penetrate the MMG and mix with more saline in-situ water (halite-saturated water derived by concentrating the Sherwood Sandstone Group water from Sellafield BH3 DET 1, (Bath et al., 2006) (see above).

```
SOLUTION 1      # Boundary Water - marine water, Millero et al., 2008
temp      25
pH        8.1
units     mg/L
density   1.02
Na        10995.7
K         407
Ca        420.3
Mg        1309
Al        0.001 Gibbsite
Si        0.001 SiO2:2H2O(am)
Cl        19737.3 charge
S(6)      923.2 as S
C(4)      21.04 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc6-Seawater&SellBH3 mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl   S(6)  C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END

SOLUTION 2    # LSSR In situ water - halite saturated Sherwood Sandstone
Group water from Sellafield BH3 DET 1, Bath et al., 2006
temp      25
pH        5.94
units     mg/l
density   1.2
Na        121193
K         560.8
Ca        1797
Mg        1174
Al        0.01171 Gibbsite
Si        44.27 SiO2:2H2O(am)
Cl        192216 charge
```

```
S(6)      790.4 as S
C(4)      15.94 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2

END

MIX 1
1 0.001
2 0.999

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

```
MIX 5
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 10
```

```
1   0.99
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

EAST LINCOLNSHIRE

7. Water pumped from the Sherwood Sandstone Group aquifer at the Welton Location (Table 22) (Smedley and Edmunds, 2002) was considered to be a potential brackish water type that could be penetrating the MMG and mixing with more saline in-situ water (Agden brine reported in Tellam, 1995).

```
SOLUTION 1      # Boundary Water - Sherwood sandstone, Welton, Lincs,
Smedley and Edmunds, 2002
temp       25
pH         7.93
units      mg/L
density    1.003
Na         2030
K          38.3
Ca         1200
Mg         291
Al         0.001 Gibbsite
Si         6 SiO2:2H2O(am)
Cl         5000 charge
S(6)       500.6 as S
C(4)       14.4 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc7-Welton&Agden Mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl S(6)  C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END
SOLUTION 2    # LSSR In situ water - Agden Brine Tellam, 1995 (result of
Simulation #2)
temp       25
pH         5.75
units      mg/l
density    1.199
Na         122261
K          104.8
Ca         1222
Mg         410.2
Al         23.59 Gibbsite
```

```
Si        14.65 SiO2:2H2O(am)
Cl        188572 charge
S(6)      1560 as S
C(4)      26.51 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2

END
MIX 1

1 0.001
2 0.999

EQUILIBRIUM_PHASES

Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000
```

```
END

MIX 5
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000
```

```
END

MIX 10
1   0.99
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

8. Water pumped from the Sherwood Sandstone Group aquifer at the Welton Location (Table 22) (Smedley and Edmunds, 2002) was considered to be a potential brackish water type that could be penetrating the MMG and mixing with more saline in-situ water (halite-saturated water derived by concentrating the Sherwood Sandstone Group water from Sellafield BH3 DET 1, (Bath et al., 2006) (see above).

```
SOLUTION 1      # Boundary Water - Sherwood sandstone, Welton, Lincs,
Smedley and Edmunds, 2002
temp      25
pH        7.93
units     mg/L
density   1.003
Na        2030
K         38.3
Ca        1200
Mg        291
Al        0.001 Gibbsite
Si        6 SiO2:2H2O(am)
Cl        5000 charge
S(6)      500.6 as S
C(4)      14.4 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc8-Welton&SellBH3 Mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl  S(6) C
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite Gibbsite SiO2:2H2O(am)
-saturation_indices Calcite Anhydrite Gibbsite SiO2:2H2O(am)

END

SOLUTION 2    # LSSR In situ water - halite saturated Sherwood Sandstone
Group water from Sellafield BH3 DET 1, Bath et al., 2006
temp      25
pH        5.94
units     mg/l
density   1.2
Na        121193
K         560.8
Ca        1797
Mg        1174
Al        0.01171 Gibbsite
```

```
Si        44.27 SiO2:2H2O(am)
Cl        192216 charge
S(6)      790.4 as S
C(4)      15.94 as C

-water    1 # kg

EQUILIBRIUM_PHASES #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE SOLUTION 2

END

MIX 1
1 0.001
2 0.999

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 2
1   0.01
2   0.99

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 3
1 0.10
2 0.90

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 4
1 0.20
2 0.80

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000
```

```
END

MIX 5
1  0.40
2  0.60

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 6
1  0.50
2  0.50

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 7
1  0.60
2  0.40

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 8
1  0.80
2  0.20

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 9
1  0.90
2 0.10

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

```
MIX 10
1   0.99
2  0.01

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END

MIX 11
1  0.999
2 0.001

EQUILIBRIUM_PHASES
Calcite 0 1000
Anhydrite 0 1000
Gibbsite 0 1000
SiO2:2H2O(am) 0 1000

END
```

9. Equilibration between standard seawater (composition from Millero et al., 2008) and selected minerals in the KCF (adopted from Section 3.6.2.2) is modelled. Ion-exchange equilibria are also considered.

```
SOLUTION 1      # LSSR Water - Example is Marine Water (Millero et al.
2008) in equilibrium with Kimmeridge clay minerals
temp      25
pH        8.1
units     mg/L
density   1.02
Na        10995.7
K         407
Ca        420.3
Mg        1309
Al        0.001 Gibbsite
Si        0.001 SiO2(am)
Cl        19737.3 charge
S(6)      923.2 as S
C(4)      21.04 as C

-water    1 # kg

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     1.084598698
Quartz      0     205.0496813
Calcite     0     27.97482266
Pyrite      0     13.00216703
Dolomite    0     6.724147281
Muscovite   0     10.13267789

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc9-SeawaterKCeq.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg  Fe Al  Si Cl   S(6) C
-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Dolomite Muscovite
-saturation_indices Kaolinite Quartz Calcite Pyrite Dolomite Muscovite

END

USE SOLUTION 1

USE EQUILIBRIUM_PHASES 1

EXCHANGE 1
X 15
```

```
-equilibrate 1

SAVE EXCHANGE 2

END

USE SOLUTION 1
USE EQUILIBRIUM_PHASES 1
USE EXCHANGE 2

END
```

10. Water from the Spilsby Sandstone aquifer (Table 22) (Edmunds et al., 2001a) was considered as a potential freshwater type that could be penetrating the KCF and mixing with in-situ water. Model KCF water is obtained from the output of the previous model, above. Ion exchange equilibria are also considered.

```
SOLUTION 1      # Boundary Water - Spilsby Sandstone, Edmunds et al., 2001a
temp      25
pH        8.7
units     mg/l
density   0.9968
Na        338 charge
K         5.6
Ca        1.8
Mg        1.3
Al        1.00E-06 Gibbsite
Si        3.2 SiO2(am)
Cl        210
S(6)      26.13 as S
C(4)      93.5 as C

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     1.084598698
Quartz      0     205.0496813
Calcite     0     27.97482266
Pyrite      0     13.00216703
Dolomite    0     6.724147281
Muscovite   0     10.13267789

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc10-Spilsby&KC mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al Si Cl S(6)  C
-molalities NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite
-saturation_indices Calcite

END

SOLUTION 2    # LSSR In situ water - marine water equilibrated with KCF
minerals & exchanger
temp      25
pH        6.165
units     mg/l
density   1.02
Na        10965.7
K         55.23
Ca        1443
Mg        816.6
```

```
Al        2.06E-05 gibbsite
Si        4.282 SiO2(am)
Cl        19721.9 charge
S(6)      920.5 as S
C(4)      86.1 as C

-water    1 # kg

EQUILIBRIUM_PHASES 2 #estimated from mineralogical composition
Kaolinite   0     1.084598698
Quartz      0     205.0496813
Calcite     0     27.97482266
Pyrite      0     13.00216703
Dolomite    0     6.724147281
Muscovite   0     10.13267789

SAVE SOLUTION 2

EXCHANGE 1
X 15

-equilibrate 2

SAVE EXCHANGE 1

END

Mix 1
1 0.001
2 0.999

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 2
1   0.01
2   0.99

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 3
1  0.10
2  0.90

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 4
1  0.20
2  0.80
```

```
USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 5
1  0.40
2  0.60

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 6
1  0.50
2  0.50

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 7
1  0.60
2  0.40

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 8
1  0.80
2  0.20

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 9
1  0.90
2  0.10

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 10
1  0.99
2  0.01

USE EQUILIBRIUM_PHASES 2
```

```
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 11
1  0.999
2  0.001

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END
```

11. Equilibration between standard seawater (composition in Millero et al., 2008) and selected minerals in the OCF (adopted from Section 3.6.3.2 of the report) was modelled. Ion exchange equilibria are also considered.

```
SOLUTION 1      # LSSR Water - Example is Marine Water (Millero et al.
2008) in equilibrium with OCF minerals
temp      25
pH        8.1
units     mg/L
density   1.02
Na        10995.7
K         407
Ca        420.3
Mg        1309
Al        0.001 Gibbsite
Si        0.001 SiO2(am)
Cl        19737.3 charge
S(6)      923.2 as S
C(4)      21.04 as C

-water    1 # kg

EQUILIBRIUM_PHASES 1
Kaolinite   0     18.17994009
Quartz      0     192.8443431
Calcite     0     40.05284133
Pyrite      0     8.964457039
Siderite    0     10.12716497
Gypsum      0     3.079615048

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc11-SeawaterOCeq.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca    Mg Al  Si Cl   S(6) C
-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Dolomite Muscovite
-saturation_indices Kaolinite Quartz Calcite Pyrite Dolomite Muscovite

END

USE SOLUTION 1

USE EQUILIBRIUM_PHASES 1

EXCHANGE 1
X 15
```

```
-equilibrate 1

SAVE EXCHANGE 2

END

USE SOLUTION 1
USE EQUILIBRIUM_PHASES 1
USE EXCHANGE 2

END
```

12. As the OCF is located stratigraphically below the KCF, the water composition on the boundary of the OCF was determined by mixing the model KCF porewater and boundary water from the Spilsby Sandstone (produced by the input file given previously). A mixture of these waters in the proportion 1:1 was considered to be a credible boundary water. Such credible boundary water is mixed with the OCF water obtained from the output of the previous model, above.

```
SOLUTION 1      # Boundary Water - 50% KCF porewater mixed with 50% Spilsby
sandstone porewater
temp      25
pH        6.41
units     mg/l
density   1.009
Na        6227
K         30.4
Ca        497.4
Mg        243.9
Al        2.17E-05 Gibbsite
Si        4.639 SiO2(am)
Cl        10000.2 charge
S(6)      474.7 as S
C(4)      95.33 as C

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     18.17994009
Quartz      0     192.8443431
Calcite     0     40.05284133
Pyrite      0     8.964457039
Siderite    0     10.12716497
Gypsum      0     3.079615048

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc12-Spilsby&KCmix(1-1)&OC mix.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca Mg Al Si Cl S(6)  C
-molalities NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Siderite Gypsum
-saturation_indices Kaolinite Quartz Calcite Pyrite Siderite Gypsum

END

SOLUTION 2    # LSSR In situ water - marine water equilibrated with OCF
minerals & exchanger
temp      25
pH        7.09
units     mg/l
density   1.02
Na        10967.8
```

```
K         406
Ca        543.5
Mg        1306
Al        5.35E-05 gibbsite
Si        4.299 SiO2(am)
Cl        19725.8 charge
S(6)      1035 as S
C(4)      16.71 as C

-water    1 # kg

EQUILIBRIUM_PHASES 2 #estimated from mineralogical composition
Kaolinite   0     18.17994009
Quartz      0     192.8443431
Calcite     0     40.05284133
Pyrite      0     8.964457039
Siderite    0     10.12716497
Gypsum      0     3.079615048

SAVE SOLUTION 2

EXCHANGE 1

X 15

-equilibrate 2

SAVE EXCHANGE 1

END

Mix 1
1 0.001
2 0.999

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 2
1   0.01
2   0.99

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 3
1  0.10
2  0.90

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END
```

```
Mix 4
1  0.20
2  0.80

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 5
1  0.40
2  0.60

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 6
1  0.50
2  0.50

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 7
1  0.60
2  0.40

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 8
1  0.80
2  0.20

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 9
1  0.90
2  0.10

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 10
```

```
1  0.99
2  0.01

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END

Mix 11
1  0.999
2  0.001

USE EQUILIBRIUM_PHASES 2
USE EXCHANGE 1
SAVE EXCHANGE 1

END
```

EAST ANGLIA

13. Due to the availability of porewater composition data for the depth of interest in the MMG in East Anglia, the porewater composition reported in Table 23 (Burley et al., 1984) is considered as a credible water composition. However, to adjust the reported water composition and make it internally consistent, a partial equilibrium model was developed taking into account the mineralogy of the rock.

```
SOLUTION 1      # LSSR Water - Summary water chemistry for the MMG,
Norfolk, depth 683 m
temp       25
pH         7.1
units      mg/l
density    1.031
Na         16700
K          240
Ca         3000
Mg         800
Al         0.001 gibbsite
Si         0.001 SiO2:2H2O(am)
Cl         31000 charge
S(6)       193.6 as S
C(4)       39.37 as C

-water     1 # kg

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Calcite 0 1000
Anhydrite 0 1000

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Cacl13-Burley_adjust.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg  Al  Si Cl   S(6) C
#-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Calcite Anhydrite
-saturation_indices Calcite Anhydrite

END
```

WESSEX BASIN

14. Due to the non-availability of porewater composition data for the depth range of interest in the KCF in the Wessex Basin, the porewater compositions reported in Table 25 for the two locations at Ashdown (Surrey) are considered as credible water compositions. However, to adjust the reported water composition and make it internally consistent, a partial equilibrium model was developed, taking into account the mineralogy of the rock.

a)

```
SOLUTION 1      # LSSR Water - Ashdown, Surrey, depth 629
temp      25
pH        7.4
units     mg/l
density   1.02
Na        13500
K         23
Ca        404
Mg        12
Al        0.001 gibbsite
Si        0.001 SiO2(am)
Cl        20590 charge
S(6)      260.7 as S
C(4)      151.6 as C

-water    1 # kg

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     1.084598698
Quartz      0     205.0496813
Calcite     0     27.97482266
Pyrite      0     13.00216703
Dolomite    0     6.724147281
Muscovite   0     10.13267789

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc14-Ashdown1adj.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg Al  Si Cl   S(6) C
#-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Dolomite Muscovite
-saturation_indices Kaolinite Quartz Calcite Pyrite Dolomite Muscovite

END
```

b)

```
SOLUTION 1      # LSSR Water - Ashdown, Surrey, depth 702
temp      25
pH        7.8
units     mg/l
density   1.012
Na        8820
K         34
Ca        200
Mg        12
Al        0.001 gibbsite
Si        0.001 SiO2(am)
Cl        13000 charge
S(6)      197.6 as S
C(4)      198.8 as C

-water    1 # kg

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     1.084598698
Quartz      0     205.0496813
Calcite     0     27.97482266
Pyrite      0     13.00216703
Dolomite    0     6.724147281
Muscovite   0     10.13267789

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc14-Ashdown2adj.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca    Mg  Al  Si Cl   S(6) C
#-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Dolomite Muscovite
-saturation_indices Kaolinite Quartz Calcite Pyrite Dolomite Muscovite

END
```

15. Due to the paucity of data for porewater compositions in OCF in the area of interest, data from a borehole in Didcot, Oxfordshire were used (Table 26 of the report). To adjust the reported water composition and make it internally consistent, a partial equilibrium model was developed, taking into account the mineralogy of the rock.

```
SOLUTION 1      # LSSR Water - Didcot depth 105m
temp      25
pH        5.6 #based on Harwell, HW4, Oxon
units     mg/l
density   1.003
Na        2860
K         73.4 #based on Harwell, HW4, Oxon
Ca        283
Mg        205
Al        0.001 gibbsite
Si        25.7 SiO2(am)
Cl        5720 charge
S(6)      532.3 as S
C(4)      24 as C

-water    1 # kg

EQUILIBRIUM_PHASES 1 #estimated from mineralogical composition
Kaolinite   0     18.17994009
Quartz      0     192.8443431
Calcite     0     40.05284133
Pyrite      0     8.964457039
Siderite    0     10.12716497
Gypsum      0     3.079615048

SAVE EQUILIBRIUM_PHASES 1

SAVE SOLUTION 1

SELECTED_OUTPUT
-file Calc15-Didcot_adj.txt
-reset false
-simulation true
-state  true
-pH true
-alkalinity true
-ionic_strength true
-charge_balance true
-percent_error true
-totals Na K  Ca   Mg  Al  Si Cl   S(6) C
#-molalities X-  NaX KX CaX2 MgX2
-activities  H+  Na+ NaCl Na(SO4)- K+ KCl K(SO4)- Ca+2 CaCl2 CaCl+
Ca(SO4)CaCO3 Mg+2 MgCl+ Mg(SO4) SO4--Na(SO4)- Ca(SO4)FeCl3- CO2 HCO3- CO3-2
-equilibrium_phases Kaolinite Quartz Calcite Pyrite Siderite Gypsum
-saturation_indices Kaolinite Quartz Calcite Pyrite Siderite Gypsum

END
```

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