# Iron Sulphides and Surface Heating: Further Engineering Considerations for the Dublin Area

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## Introduction

In comparison with other documented cases of sulphate-related heave, notably in the UK and Canada, the onset of heave following construction has been particularly quick in Ireland. Hawkins (2012) presented a model to explain this rapid onset of heave, considering the development of ferrous sulphates around oxidising iron sulphides as well as the probable role of pyrrhotite. The Pyrite Panel Report (2012) also noted this rapidity, suggesting that Ireland's mild climate and the stockpiling of pyritic aggregates were influential factors.

This chapter discusses recent research which indicates that there are a number of characteristics of the iron sulphides within the Carboniferous rocks of the Dublin area which have not been fully appreciated. The importance of temperature during deep burial in the formation and the occurrence of pyrrhotite (a less stable form of iron sulphide) are reviewed. Case histories from a number of countries are presented to illustrate the involvement of pyrrhotite in sulphate-related heave and attack on concrete.

The chapter highlights the significance of the near-surface temperatures in the Dublin region where heat emanates from the Leinster Granites to the south and thermal springs issue from the Carboniferous strata. Localised rising groundwaters at temperatures of up to 25 °C are an important consideration when assessing the rate of oxidation of iron sulphides and hence sulphate-related heave. In addition, raised temperatures are also likely to be present in the overlying Dublin Boulder Clay, particularly where there is only a limited cover over rocks containing faults/

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master joints. New evidence for a variety of textures/structures in pyrite/pyrrhotite from the Dublin area is presented and the implications of this for the rate of oxidation are considered.

## The Nature and Identification of Pyrrhotite

Cases of sulphate heave and sulphate attack due to the oxidation of pyrite in fill or natural ground are well documented and discussed further elsewhere in this volume. However, the role of pyrrhotite, a highly reactive iron mono-sulphide, is under-appreciated and remains poorly understood, although there are published accounts of the involvement of pyrrhotite oxidation in damage to buildings and civil structures from as long ago as 1919 (Fiskaa et al. 1971).

Pyrrhotite has been described as "one of the most hazardous" inclusions in concrete aggregate (Chinchón et al. 1990). Some engineering Standards have recognised these problems and recommended special precautions in the form of very low total sulphur acceptance criteria when pyrrhotite is identified. However, bearing in mind the speed of reactions with pyrrhotite, current standardised methods of assessment and tolerance criteria may be inappropriate.

### Mineralogical Background and Identification

Pyrrhotite, an iron mono-sulphide with the general formula $Fe_{(1-x)}S$ (x between 0 and 0.125), is the second most abundant iron sulphide. When observed in hand specimen it appears bronze to dark brown in colour, often with a metallic lustre (Fig. 1).

**Fig. 1** Hand specimen fragment with coarse pyrrhotite grains from Canada

High temperature phases typically crystallise in the hexagonal system whilst low temperature phases are typically monoclinic. Habits include tabular forms as well as anhedral "chunks". Pyrrhotite will decompose in HCl and has a hardness of 3.5–4. In thin section, it is weakly pleochroic and strongly anisotropic (Vaughan 2011). Some polytypes exhibit weak magnetism.

## Chemical Testing

Routine testing for sulphur species in aggregate/fill material is undertaken according to EN 1744-1:2009 (BSI 2010). The tests described include those for total sulphur, acid soluble sulphides, acid soluble sulphates and water soluble sulphates. As the total sulphur test involves the addition of HCl to the sample, pyrrhotite will be dissolved, although its composition will be accounted for in the final percentage sulphur value.

The EN 1744-1:2009 test for acid soluble sulphides involves decomposition of the sample by HCl and conversion of the dissolved sulphides to hydrogen sulphide. The gaseous hydrogen sulphide reacts with an ammonium-bearing zinc sulphate solution, causing the precipitation of the zinc sulphide. The sulphide content in zinc sulphide is then calculated and expressed in percent sulphur.

The use of acidified chromium results in the digestion of pyrite and marcasite in the test described above (Czerewko et al. 2003; BSI 2010). As pyrite is not soluble in HCl, whereas pyrrhotite is, by omitting the chromium the pyrrhotite would be dissolved in the HCl, leaving the pyrite. It is therefore possible this method could be modified to determine the mono-sulphide content (i.e., pyrrhotite). Potential problems could arise from the dissolution of pyrite due to other reagents, the dissolution of other acid soluble sulphides (such as greigite and mackinawite) or only partial dissolution of the mono-sulphides (Czerewko et al. 2003; Reid et al. 2005).

A simpler procedure for identifying mono-sulphides was proposed by Tuttle et al. (1986) whereby the $H_2S$ gas produced during dissolution of the sample by HCl is analysed directly (rather than further reacted as in the BSI 2010 method). The gas is analysed quantitatively by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

No standardised test exists to determine the pyrrhotite content of a sample. However, further research is being undertaken into a method which can simply and reliably quantify the amount of pyrrhotite within a test sample. Although attempts have been made to estimate the "equivalent pyrite" content of a sample based on various test results, for example in the Canadian assessment procedure CTQ-M200 (Comité Technique 2001), to date no similar calculation exists to estimate the "equivalent pyrrhotite". However, as discussed in Hawkins (2013 this book), there are problems with the reliability of such estimations, which involve a number of assumptions.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) is a technique which allows identification based on morphology (Fig. 2) and elemental analysis. Careful sample preparation and appropriate coating is essential for quantitative analysis. An electron microprobe can also be used for quantitative identification.

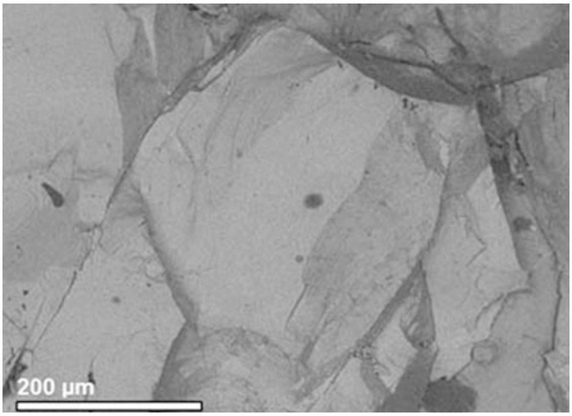


**Fig. 2** SEM image of hexagonal pyrrhotite from Sudbury, Canada

However, as pyrite and pyrrhotite comprise only iron and sulphur, distinguishing one grain from another can be difficult. For confirmation, the Fe/S ratio (by weight) is required. For idealised pyrite, the ratio is 0.87. Pyrrhotite exhibits a range of compositions based on the $Fe_{1-x}S$ formula. Assuming x values between 0 and 0.125, the calculated end-member compositions are given in Table 1. It can be seen that weight percent Fe/S ratios for pyrrhotite range from 1.52 to 1.74, which can be used as guidance for identification using EDS results.

**Table 1** Pyrrhotite compositions and Fe/S ratios for end-member values of x

| Value of x | Ideal compound | Atomic Fe:S | Wt % Fe/S ratio |
|---|---|---|---|
| 0 | FeS | 1:1 | 1.74 |
| 0.125 | $Fe_7S_8$ | 0.875:1 | 1.52 |

### X-ray Diffraction

X-ray diffraction (XRD) is another long-established technique used to identify pyrrhotite, as reported by Tagnit-Hamou et al. (2005) for aggregate analysis. However, Hammarstrom and Smith (2002) note the failure of XRD to identify pyrrhotite despite its observation in thin section. Indeed, these authors have recorded that alteration to pyrite and goethite may give rise to major XRD peaks which mask the presence of pyrrhotite. Alternatively the XRD preparation processes may destroy pyrrhotite such that its presence is undetectable. Ideally, samples should be prepared with minimal disturbance and tested immediately after recovery to reduce the extent of pyrrhotite oxidation.

## *Occurrence and Formation of Pyrrhotite*

Pyrrhotite is found in a wide range of igneous rocks including gabbro (Duchesne and Fournier 2011), diorite (Kelly and Zumberge 1961), basalt (Xie et al. 2010) and granite (Gottesmann and Wirth 1997). It is ubiquitous in low-grade metamorphosed shales (Aubourg et al. 2004). Occurrences in slates and meta-shales include the Welsh Cambrian slates (Fuller 1964), Scottish Dalradian Ballachulish slates (Hall 1982) and Norwegian Cambrian Alum Shale (Abreham 2007). Up to 15 wt % pyrrhotite is present in the Cambro-Ordovician Halifax Formation shales of Nova Scotia (Fox et al. 1997).

Although pyrrhotite has been less reported in sedimentary rocks in the UK it has been found in the Pleistocene swamp deposits of the Lea Valley, England (Davies 1912), the Carboniferous Coal Measures of Wales (Simpson and Stuart 1934) and the Brownstones of the Devonian Old Red Sandstone sequence in the Merthyr Tydfil area of South Wales (Barclay et al. 1988). Pyrrhotite is also found within hydrothermal vein deposits in sedimentary/meta-sedimentary sequences, such as in the Exmoor region in south west England (see later).

### Formation

Pyrrhotite formation in igneous rocks occurs via crystallisation from magma which is rich in both iron and sulphur; it is not considered here.

Although uncommon as an authigenic phase in sediments, pyrrhotite can form in abundance at the expense of pyrite during low grade metamorphism (including burial) of pyritic strata. As discussed below, pyrrhotite formed in this manner has caused numerous engineering problems. The main formation mechanisms for pyrrhotite in sedimentary and meta-sedimentary rocks include:

1. Detrital
2. Authigenic
3. Metamorphic desulfidation of pyrite
4. Precipitation from sulphidic ore fluids

Detrital pyrrhotite has been reported by Shi et al. (2001) who observed large and irregular shaped grains in a loess section at Znojmo (Czech Republic), in association with galena. Horng and Roberts (2006) argued that pyrrhotite in a section of Pleistocene sediments in Tsailiao-Chi (Taiwan) originated from metamorphic rocks. These reports are quite surprising considering the chemically unstable nature of pyrrhotite, which would make it unlikely to survive erosion and transportation.

In sedimentary rocks, iron sulphides are generally believed to form authigenically in anoxic subaqueous conditions. Preservation of pyrrhotite may be aided by the consumption of $H_2S$ in low permeability sediments (Roberts and Turner 1993).

Bastiansen et al. (1957) observed the formation of pyrrhotite when pyritic shale was heated to c. 300 °C. The conversion was later described as a thermal decomposition effect and found to occur at temperatures as low as 200 °C (Lambert 1973; Butcher and Rowson 1995). This process represents a loss of sulphur and was termed "desulfidation" by Ferry (1981). It is thought to be aided by the presence of carbon-bearing phases (Lambert 1973). Ferry (1981) proposed reaction (1):

$$2FeS_2 + 2H_2O + C_{(graphite)} \rightarrow 2FeS + 2H_2S + CO_2 \qquad (1)$$

The transformation has been confirmed by Pitcairn et al. (2010), who studied the conversion of pyrite in New Zealand schists of various grades and demonstrated that as temperature increases, pyrrhotite abundance increases at the expense of pyrite.

Pyrrhotite may also be precipitated from sulphidic fluids during ore concentration. In massive sulphide deposits, chalcopyrite and pentlandite are also typically present, while in veins/bedding plane coatings it can be found with marcasite, chalcopyrite, sphalerite and other metal-sulphides. Major deposits of this type exist in Sudbury, Canada, where pentlandite is mined for nickel and pyrrhotite is discarded to waste tailings (Becker, Bradshaw and de Villiers 2011). At the Phoenix Mine in Botswana, pyrrhotite is mined for nickel hosted within pentlandite intergrowths (Becker et al. 2011).

Elsewhere, pyrrhotite from massive sulphide deposits has been mined for use in the production of sulphuric acid, such as at the now abandoned Kettara Mine in Morocco. More than 5 million tons of Carboniferous-hosted pyrrhotite ore was mined here between 1964 and 1981 (Hakkou et al. 2008). The mining left vast areas of tailings which have contributed to a major acid drainage problem. The mine was ultimately closed due to acid corrosion of the plant equipment.

## *Oxidation and Reactivity*

Pyrrhotite is unstable under atmospheric conditions, making it prone to oxidation. Cai et al. (2005) suggest that oxidation occurs as early as the blasting stage during aggregate sourcing. Like pyrite, pyrrhotite can oxidise when exposed to oxygen and moisture (2):

$$Fe_{1-x}S + \left(2 - \frac{x}{2}\right)O_2 + xH_2O \rightarrow (1 - x)Fe^{2+} + SO_4^{2-} + 2xH^+ \qquad (2)$$

The oxidation of pyrrhotite can produce ferrous iron, sulphate ions and hydrogen ions, which may combine to form ferrous sulphates and sulphuric acid (Seal and Hammarstrom 2003). From a study of mine tailings, Georgopoulou et al. (1995) report that up to 1.1 tonnes of sulphuric acid can be produced by a single tonne of pyrrhotite. Equation (2) shows that where the value of x in the pyrrhotite composition is at a maximum (i.e., 0.125 or the monoclinic form), there is a greater amount of $H^+$ ions released, and hence the acidity generated is at a maximum.

The sulphuric acid generated can react with any remaining pyrrhotite to produce $FeSO_4$ (Fiskaa et al. 1971). If hydrated ferrous sulphate is formed instead, Casanova et al. (1996) have shown that a volume increase of over 180 $cm^3$ per mol of pyrrhotite ($x = 0.125$) is possible. Recent work has shown that the formation of ferric hydroxide from pyrrhotite may involve an expansion of up to 34 %, compared to only 13 % for pyrite (Oliveira et al. 2013). Where calcite exists in the host rock, it may react with the released sulphuric acid to produce gypsum, with additional expansion (Bérard et al. 1975).

In addition to oxygen-bearing products, Hammarstrom and Smith (2002) report that pyrrhotite oxidation can yield pyrite. It is possible that pyrite may replace pyrrhotite, leaving a pseudomorph which has the hexagonal habit (e.g., Fig. 2) of pyrrhotite.

The $Fe_{(1-x)}S$ structure is a “defect structure” with less iron than the ideal FeS stoichiometry. Iron vacancies are thought to give rise to instability and influence oxidation (Nicholson and Scharer 1993). In terms of crystallography, the majority of workers suggest that monoclinic pyrrhotite is more reactive than hexagonal forms (e.g., Becker 2009). This implies that the form likely to be encountered in low grade metamorphosed rocks may be more prone to oxidation.

There are many published accounts of factors believed to influence pyrrhotite oxidation. As with pyrite, oxygen, moisture, $Fe^{3+}$, temperature, presence of bacteria and surface area all aid oxidation (Janzen et al. 2000; Belzile et al. 2004; Oliveira et al. 2011). Many workers suggest that alkaline conditions favour faster oxidation (e.g., Truche et al. 2010) although the build-up of oxidation products may limit reactivity while *Thiobacilli* bacteria aid oxidation at a low pH (Bhatti et al. 1993).

Pyrrhotite can oxidise up to 100 times faster than pyrite under atmospheric conditions (Nicholson and Scharer 1993). It will also oxidise faster than pyrite in the presence of *Thiobacilli* bacteria (Bhatti et al. 1993). In addition, recent laboratory work by Chinchón-Paya et al. (2012) has shown that pyrrhotite can generate more sulphates than pyrite. The presence and oxidation of pyrrhotite in rock may also catalyse the oxidation of pyrite (Bastiansen et al. 1957; Moum and Rosenqvist 1959).

## *Case Studies*

A review of the literature highlights a number of accounts of structural distress which involved pyrrhotite.

### Oslo and the Alum Shale

Numerous problems have occurred in Oslo where concrete has come into contact with the Norwegian Alum Shale, a low grade Cambro-Ordovician carbonaceous black shale containing pyrrhotite (Hagelia 2011). Problems were noticed as early as 1919 and became so severe that the "Alum Shale Committee" was established in 1943 (Fiskaa et al. 1971). The most renowned example is the sulphate attack on an underground concrete shelter founded in Alum Shale (Moum and Rosenqvist 1959). It is reported that within only nine months, acidic water associated with weathered pyrite and pyrrhotite had degraded the concrete to "mush". Similar problems were reported where aggregate containing pyrrhotite was used. Damage was noted where pyrrhotite mineral and pyrrhotite sulphur contents in the aggregate were as low as 0.01 % and 0.071 wt % respectively (Bastiansen et al. 1957; Hagelia 2011). The Alum Shale Committee concluded that aggregates with pyrrhotite sulphur contents below 0.001 % were safe (reported in Hagelia and Sibbick 2009).

### Spanish Experiences

As early as 1962, the potential for problems arising from pyrrhotite in aggregate were published in the Spanish literature (Vidal 1962). Between 1970 and 1972, severe and rapid degradation of concrete used in buildings in the Maresme region of Barcelona was attributed to the oxidation of sulphides (Vazquez and Toral 1984). Low grade dark Silurian shale had been included in the aggregate, which was confirmed by SEM to contain pyrrhotite. Samples from the source quarry were described as having undergone contact metamorphism, producing graphite (Chinchón et al. 1995). Pyrrhotite was identified in layers and disseminations within the shale while gypsum was observed on discontinuities (Chinchón et al. 1995). During the 2000s the concrete in several dams in the Spanish Pyrenees was observed to have cracked and deteriorated. In all cases, the aggregate used in the concrete was sourced from local quarries. Araujo et al. (2008) used optical microscopy, SEM, XRD and XRF to investigate the materials. Needle-like ettringite was found within the cracked concrete and pyrrhotite, pyrite, gypsum and jarosite were all observed within the quarry material. Araujo et al. (2008) concluded that the oxidation of pyrrhotite had produced sulphates which resulted in expansion of the concrete.

## Swedish Experiences

During the 1960s many buildings in the Östersund area suffered damage and deterioration (Martna 1970; Jangdal 1971). The cause was not appreciated at first, but was later attributed to the swelling of pyrrhotite-bearing shale.

A number of Swedish dams also experienced cracking during the 1960s (Fristrom and Sallstrom 1967). In one case, up to 10 % “magnetic pyrite” (pyrrhotite) was found within the concrete aggregate. The oxidation of both pyrrhotite and pyrite led to major swelling and cracking of the dam concrete, as well as the formation of calcium alumino-sulphates. Ultimately the damaged zones of the dam required replacement.

Martna (1970) reported sulphate attack on the concrete of a hydro-electric station in Stornorrfors. Part of the power station extended some 100 m below ground, within pyrrhotitic gneiss. Sulphuric acid produced during the oxidation of the pyrrhotite severely degraded the concrete lining.

## Canadian Experiences

Many pyrite and pyrrhotite problems have been reported from Canada in the last 40 years. The earliest distress which involved pyrrhotite oxidation was recognised by Bérard et al. (1975), who discussed the deterioration of concrete house foundations within only two years after construction. In the areas of distress, it was found that black Utica Shales had been used as concrete aggregate. Analysis by XRD, traditional microscopy, electron microprobe and chemical methods identified around 4.5 % pyrrhotite within the aggregate. Pyrrhotite was observed both as very fine grains and as clusters and veinlets (Bérard et al. 1975). Oxidation of pyrrhotite in the presence of carbon and the formation of gypsum were considered to be the causes of the distress.

In February 2012, Robert Aubin (QC) referred to a new “pyrrhotite crisis” in the Trois Rivières area of Québec, stating that over 1,000 homes had “disintegrating foundations” due to the use of aggregate containing pyrrhotite. Damage was manifested as concrete degradation and cracking as well as floor slab heaving (PCC 2012). Repair costs are estimated at around $200,000 per home. However, some 10 years ago around 40 homes in this area also suffered pyrrhotite problems in the form of degradation of basement concrete (Coalition Proprio-Béton 2012). In these cases, locally sourced pyrrhotite-bearing gabbro had been used as concrete aggregate.

Investigations into damaged foundations in Trois Rivières were also published by Tagnit-Hamou et al. (2005) and later by Duchesne and Fournier (2011). Visible damage was observed as early as two years post-construction. Petrographic analysis indicated that the aggregate was again gabbro with up to 7 % pyrrhotite and pyrite—the pyrrhotite being more oxidised than the pyrite. Oxidation of the iron sulphides and the development of gypsum and ettringite were identified as the causes of the deterioration. Remediation involved complete foundation replacement.

## The "Mundic" Problem

The term "Mundic" derives from a Cornish word for pyrite and the problem refers to a legacy of concrete degradation in Devon and Cornwall due to the presence of sulphides within the concrete aggregate (Bromley and Pettifer 1997). Whilst much of the deleterious aggregate was sedimentary or sulphidic mine waste, igneous rock was also quarried. Pyrrhotite was identified in quarried slate from Delabole and gabbro from Porthoustock, S W England.

The meta-dolerite quarry at Penlee (Newlyn, Cornwall) was used to source aggregate for concrete blocks and foundations. Detailed petrography of the dolerite identified pyrrhotite among other sulphides (Bromley and Pettifer 1997). Deteriorated concrete blocks were often found to contain the oxidation products of these sulphides, including gypsum within voids. The Penlee Quarry eventually closed due to the excessive sulphide levels.

## Switzerland

Schmidt et al. (2011) reported on a Swiss dam with cracked and deteriorated cement due to the use of concrete containing schist aggregate. Analysis with SEM and EDS confirmed the presence of pyrrhotite with an oxidised exterior. The iron sulphide content in the aggregate was reported to be 0.28 %, of which 80 % was pyrrhotite. It was suggested that only 30 % of the iron sulphides in the aggregate had reacted within 40 years. Pyrrhotite was found to be more extensively oxidised than pyrite.

## Central Himalayas

In 1978, red-brown water was observed to have seeped from cracks in the Pandoh Dam in the Central Himalayas (Dubey et al. 2004). Petrographic analysis of the local bedrock revealed pyrrhotite both as disseminated grains and infilling fractures, as well as iron hydroxides in the low to medium grade schist. Gypsum and ettringite were identified by XRD in a precipitate of the red-brown water. The workers concluded that the damage resulted from sulphide oxidation and the formation of gypsum and ettringite.

## Scotland

Concrete degradation in a Scottish bridge in Strathclyde was reported by Macleod et al. (1990). Pitting and discolouration of the concrete was observed, in addition to a coating of mineral precipitates. Petrographic assessment of the concrete by stereo microscopy identified both pyrrhotite and pyrite within the dolerite aggregate. XRD analysis also revealed ettringite needles and gypsum within the concrete cavities. It was concluded that expansion had occurred due to the formation of sulphates and iron hydroxides from the oxidation of sulphides in the concrete aggregate.

### South Africa

Damage to houses in South Africa in the form of external wall cracking and heaving of the ground-bearing floor slabs was reported by Oberholster et al. (1983). Petrographic examination and XRD analysis of defective concrete blocks confirmed the aggregate used contained both pyrrhotite-bearing black shale and gold mine spoil. Gypsum developed as a consequence of the oxidation of the iron sulphides and ultimately thaumasite formed due to the reaction of gypsum with cement components. The aggregate was found to have a total sulphur content of 1.44 % S corresponding to a total potential sulphate content of 4.3 % $SO_4$ (Hobbs 2003).

Similar problems in Windhoek, Namibia were later noted by Davies and Oberholster (1988). Iron staining and pop-outs were observed on ash–cement brick walls in houses less than a year old. Petrographic analysis revealed the presence of black sulphurous nodules within the bricks, which had been sourced from the burnt-coal waste of a nearby power station. The use of SEM and XRD confirmed that the nodules were rich in iron sulphides, including pyrrhotite.

Samples of the damaged brick were later stored above water inside sealed containers. The storage room environment was maintained at around 38 °C with a relative humidity of approximately 100 %. Over the course of 93 days the samples were seen to expand, in one case fracturing the brick. XRD analysis of the broken sample identified pyrrhotite, which when tested again two weeks later had oxidised to melanterite, a hydrated ferrous sulphate. Davies and Oberholster (1988) suggest that the main damage had resulted from iron sulphide oxidation, triggered by a recent wet season which allowed water to enter the bricks and oxidise the pyrrhotite.

## *Aggregate/Concrete Standards and Pyrrhotite*

In the light of the problems caused by the presence of pyrrhotite in aggregate and fill, various Standards have set specific criteria for total sulphur (% S) when pyrrhotite is identified (Table 2). The tolerance is often considerably less than when pyrrhotite is believed to be absent, reflecting the highly reactive nature of this mineral. As seen from Table 2, the allowable total sulphur within aggregate where pyrrhotite is identified is between 2.5 and 10 times lower than if pyrrhotite were absent.

Early work by Hagerman and Roosaar (1955) suggested that an upper limit of 1 % pyrrhotite was acceptable in coarse aggregates but Bastiansen et al. (1957) reported damage for pyrrhotite contents in aggregate as low as 0.01 %. The Alum Shale Committee was even more cautious, suggesting that if pyrrhotite was

**Table 2** Total sulphur criteria for pyrrhotite-bearing aggregates (compared to those devoid of pyrrhotite), for various Standards across Europe

| Standard | Pyrrhotite present (% S) | Pyrrhotite absent (% S) |
|---|---|---|
| EN 13242:2002 + Al:2007 (BSI 2008a)<br>(Aggregates for civil engineering and road construction) | $\leq 0.4$ | $\leq 1$ |
| SR 21 (2004; 2007)<br>(Irish guidance on the use of EN 13242) | $\leq 0.4$ | $\leq 1$ |
| EN 12620:2002 + Al:2008 (BSI 2008b)<br>(Aggregates for use in concrete) | $\leq 0.1$ | $\leq 1$ |
| EHE-08 (2008)<br>(Spanish use of concrete aggregates) | $\leq 0.1$ | $\leq 1$ |

present, only aggregates with sulphur contents below 0.001 % were safe. In view of this, it is not surprising that some Standards have stipulated very low total sulphur criteria where pyrrhotite has been identified. However, EN 12620:2000 + Al 2008 and EHE-08 have been criticised for the low sulphur tolerance. It has been suggested that the upper limit of 0.1 % S is unnecessarily low and could rule out suitable aggregates (Chinchón-Paya et al. 2012).

## *Pyrrhotite in South West England*

As noted above, the report on the Mundic problem (Anon 1997) implicated pyrrhotite as a contributor to the concrete degradation and indicated its presence within igneous and metamorphic rocks. A review of the literature has highlighted that pyrrhotite in south west England is more abundant and widespread than originally appreciated (Fig. 3).

The geology of the region comprises a predominantly Devonian and Carboniferous succession of siliciclastic-argillaceous rocks into which five major granite bosses intruded during the Permian (Edmonds et al. 1969). These granites are connected at depth to form the Cornubian Batholith and their emplacement was associated with alteration and metamorphism of the country rock (typically extending 5 km from the granite outcrop).

In Devon and Cornwall pyrrhotite was formed in four main situations. In the groups discussed below the numbers refer to Fig. 3:

1. Within igneous rock (7, 12, 19, 20)
2. Within massive veins and ore mineralisation (6, 9, 10, 13–18)
3. Within aureoles, not associated with mineralisation (3, 4, 5)
4. Outside aureoles, not associated with mineralisation (1, 2, 8, 11)

Pyrrhotite is a common accessory phase in igneous rocks hence the localities in group one are expected. The majority of occurrences are associated with mineral veining (group two). Mineral ores and veins in south west England are generally

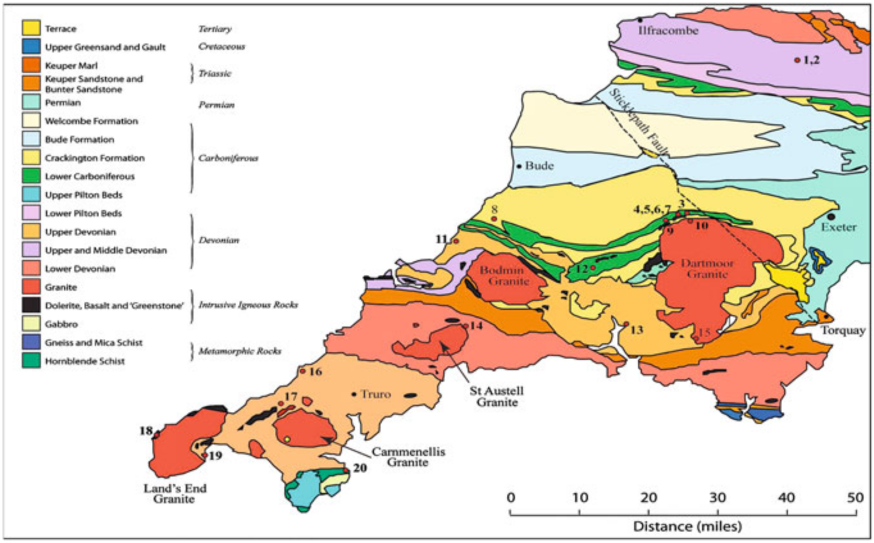


**Fig. 3** Approximate locations of pyrrhotite in Devon and Cornwall (numbered 1–20). Map adapted from Edmonds et al. (1969)

accepted as having formed from fluids associated with the cooling of the granites. The flow of metal-rich fluids along faults and fractures produced veins known as lodes (Edmonds et al. 1969).

The localities in group three include contact metamorphosed rocks and those within the granite aureoles. Here pyrrhotite is found within hornfels and meta-chert formations, in disseminated granular form, generally below 0.1 mm in size (Edmonds et al. 1968). Localities 3 and 5 are sited within the Carboniferous Teign Chert Formation which includes numerous bands of (probably pyritic) black meta-shale. Pyrrhotite formation in these rocks may have occurred by conversion of pyrite during metamorphism, as has been proposed for the Exmoor area.

Group four localities are outside any metamorphic aureole. Pyrrhotite was observed within slates at each of these localities and granite has been discounted as the source for localities 1 and 2 (Bott et al. 1958). Instead, Jones et al. (1987) favour fault-facilitated mineralisation. More probably, the pyrrhotite was formed at these locations by the metamorphic transformation of pyrite (Leveridge et al. 2002).

## *Pyrrhotite and the Irish Problems*

The rapidity with which distress has occurred in Dublin where ground-bearing floor slabs have been founded on aggregate containing iron sulphides was discussed by Hawkins (2012) who noted that the development of a ferrous sulphate rim around oxidising iron sulphides results in a previously unappreciated initial expansion. Hawkins also postulated that pyrrhotite may in some way contribute to the speed at which the expansion has occurred in the Dublin area. Subsequently, the report of the Pyrite Panel (2012) suggested a number of other factors which may have accelerated heave including:

1. The relatively mild climate of Dublin (compared to Québec for example)
2. The exposure of fill to poor weather prior to use, triggering oxidation

## Distribution of Pyrrhotite in Ireland

The Pyrite Panel Report (2012) states that "Pyrrhotite is present only in specific geologic environments in Ireland of which there are relatively few." The Geological Survey of Ireland (GSI) database of Irish mineral occurrences was consulted for the preparation of the Pyrite Panel Report. This database identifies only nine localities for pyrrhotite—around 0.1 % of all the mineral occurrences recorded. However, a review of the literature and other mineral databases highlighted a further 15 localities, giving a total of 24 for Ireland (Fig. 4). In addition to these mapped localities, it has been proposed that pyrrhotite in black shale is responsible for high conductivity anomalies in central Ireland (Rao et al. 2007). Furthermore, the Navan ore body is also suspected to contain pyrrhotite.

The pyrrhotite occurrences noted in Fig. 4 can be grouped as follows:

1. Within igneous rock (2, 4, 6, 7 and 10)
2. Within sulphide deposits, veins, lodes or ores (5, 8, 9, 11–15 and 17–24)
3. Within metamorphic aureoles, not associated with mineralisation (1, 3 and 16)

Of these 24 localities, seven are within Carboniferous rocks and in general these appear to be located towards the edges of the Carboniferous outcrop, i.e., at the margins of the original depositional basin. The majority of these seven localities are shale or carbonate-hosted ore bodies, including those at 18, 20 and 21 in the Silvermines District where mineralisation is associated with the Silvermines Fault system.

Contact metamorphism of Carboniferous rocks in Ireland is not as extensive as that observed in the south west of England, as the major igneous intrusions of Ireland pre-date the Carboniferous period. Minor, localised metamorphism has occurred at locality 3 where Tertiary dykes intruded into calcareous shales. Whilst there are no available reports of pyrrhotite within the Irish Carboniferous rocks in modes other than vein type or contact metamorphic phases, it could also have been incorporated as detrital grains during deposition or formed by regional/heating/burial of pyrite.

Heating of pyritic mudrocks to in excess of 200–250 °C has been shown to produce pyrrhotite, particularly when carbon-bearing phases are present. A

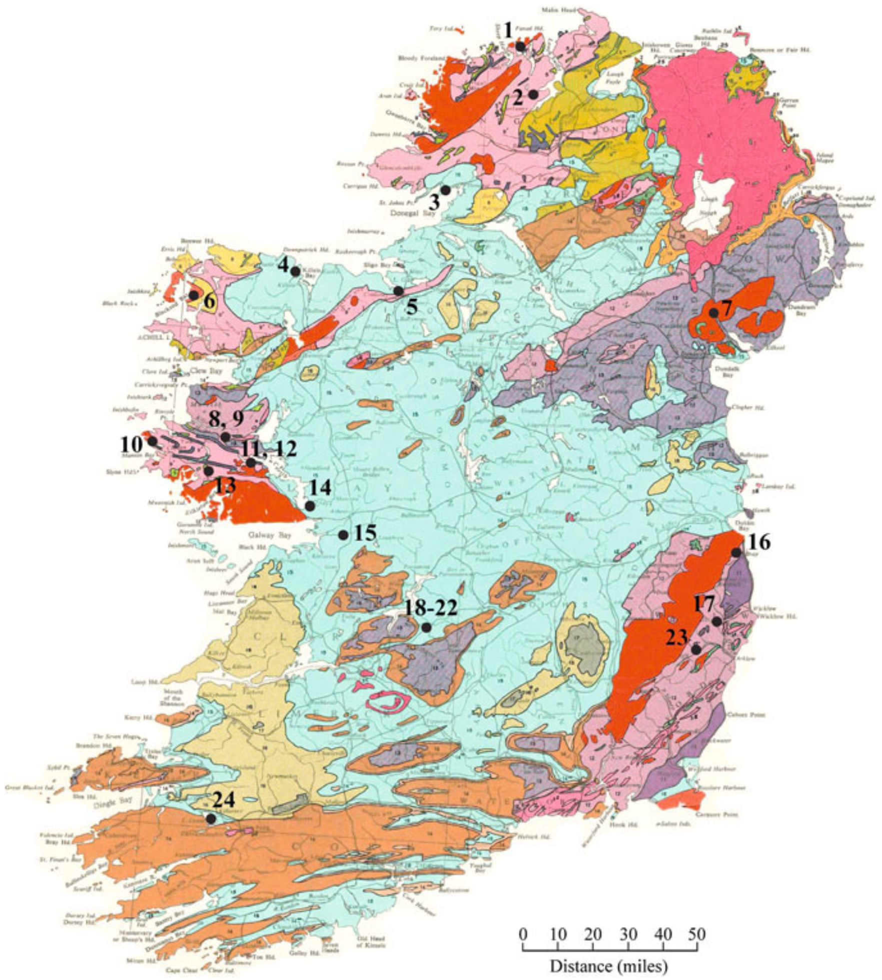


**Fig. 4** Approximate locations of pyrrhotite in Ireland; map after Dunham (1969)

number of studies, including those on Irish conodont alteration, suggest that temperatures exceeded 250 °C in the Carboniferous rocks, due to burial alone (Jones 1992; Clayton et al. 1989). Recent work by Goodhue and Clayton (2010) on thermal maturity indicators has even suggested that burial geothermal gradients in Carboniferous strata offshore of Dublin may have reached 115 °C/km. Clearly only a few kilometres of burial would be required to reach conditions where pyrrhotite could form.

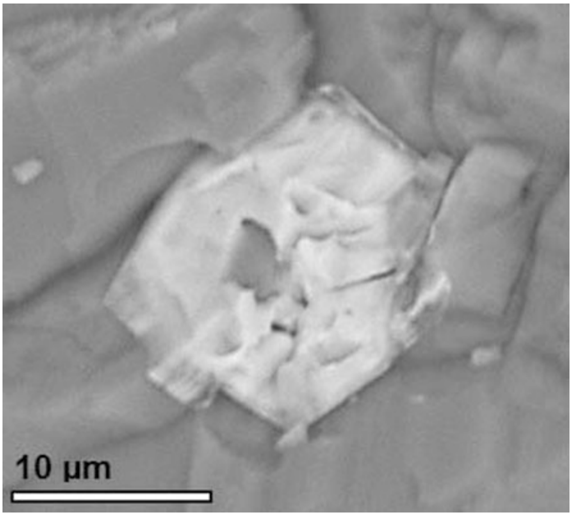
## Pyrrhotite within Carboniferous Calcareous Mudrock in the Dublin Area

When petrographic analysis was undertaken on fill which had been removed from beneath a damaged structure in north Dublin, in addition to pyrite, pyrrhotite was identified by SEM and EDS. Iron-sulphur (wt %) ratios were in the approximate range of 1.5–1.7, confirming a pyrrhotitic composition. Unusually, however, the morphological form of this pyrrhotite was framboidal. Framboidal habits are typical of pyrite. Pyrrhotite with a framboidal texture is rare, but has been observed in Texan lignite deposits (Aleksandrov and Kamneva 1976). As the central core of the mineral often remains pyritic, it is possible that framboidal pyrrhotite is associated with the conversion of pyrite to pyrrhotite.

Pyrrhotite displaying a characteristic habit was also identified by SEM–EDS within samples of the Carboniferous Tober Colleen Formation (TCF) from the Baytown area, Fingal (Fig. 5). Several sub-hexagonal grains less than 30 μm in size were identified within a calcite vein, particularly at calcite grain boundaries. On first examination, the grain shown in Fig. 5 had an iron-sulphur ratio of 1.6. After only three weeks of exposure to the atmosphere the composition was checked and confirmed to be pyritic, i.e., the pyrrhotite had converted back to the more stable iron sulphide.

Sub-hexagonal grains with pyritic compositions are common within the TCF samples (Fig. 6). These are believed to be pseudomorphs after pyrrhotite and may have formed through oxidation of pyrrhotite, as recently as during SEM preparation. In addition to burial heating, the Carboniferous rocks of Dublin underwent deformation during the Variscan Orogeny. Rotation of fault-bound blocks in the Dublin Basin produced upright to tight folding in the Chadian-Brigantian rocks (Hitzman 1999).

**Fig. 5** SEM image of a sub-hexagonal iron sulphide with a pyrrhotite composition from a borehole core, N. Dublin



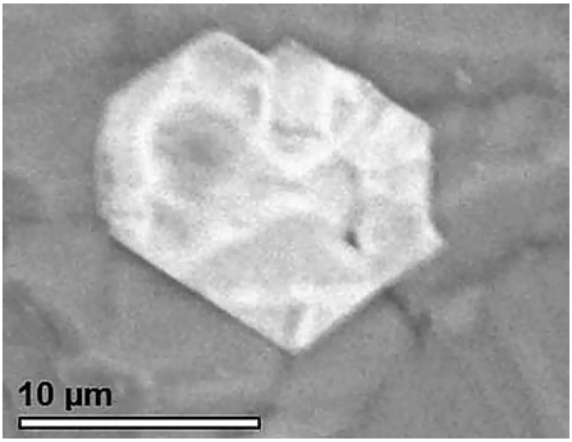


**Fig. 6** SEM image of sub-hexagonal pyrite—probable pseudomorph after pyrrhotite from a borehole core, N. Dublin

The TCF in general comprises dark, sometimes black, pyritic calcareous mudstones and minor limestones (McConnell et al. 2001; Strogen et al. 1990). The TCF itself is known to have experienced deformation which is manifest as open folding and pressure solution cleavage (McConnell et al. 2001). As it is likely the TCF experienced burial temperatures in excess of 250–300 °C, it is not unreasonable to suggest that pyrrhotite may have formed at the expense of pyrite, especially as the dark shales probably contain carbon, which would aid the conversion.

Vein-type pyrrhotite may be the more common mode of occurrence in these rocks, particularly considering the abundance of shale-hosted sulphides in the Irish Carboniferous strata. Most of the Irish Carboniferous zinc deposits comprise abundant massive sulphide lenses associated with major faults (Hitzman 1999). It is likely that faulting played an important role in the distribution of the sulphides. Unfortunately, the identification of pyrrhotite and estimation of its abundance in these rocks is problematic as it appears to oxidise quickly.

## Framboidal Pyrite from the Dublin Region: Implications for Oxidation

The framboidal form of pyrite is particularly common within the Carboniferous mudrocks of the Dublin area. Framboids and their formation have been the subject of much study and debate, but they are frequently described as sub-spherical clusters of uniformly sized and shaped pyrite microcrystals. They are typically less than 50 μm in diameter with individual microcrystals as small as 0.2–0.5 μm in diameter.

## *Pyrite Framboids from the Baytown Area*

Samples of Carboniferous calcareous mudrock were obtained from core recovered from a 20 m deep borehole at Baytown, north of Dublin. Small (<10 mm) fragments were selected at regular depth intervals and resin-mounted into thin walled sample rings. Each sample was polished to <1 μm using an oil-based lubricant to minimise exposure to moisture. Samples were then coated with approximately 20 nm of carbon to provide a conductive surface for examination. A Hitachi S-3500 N SEM equipped with an EDS detector and a JEOL JXA 8530F electron microprobe, both based at the University of Bristol, were used for imagery and quantification.

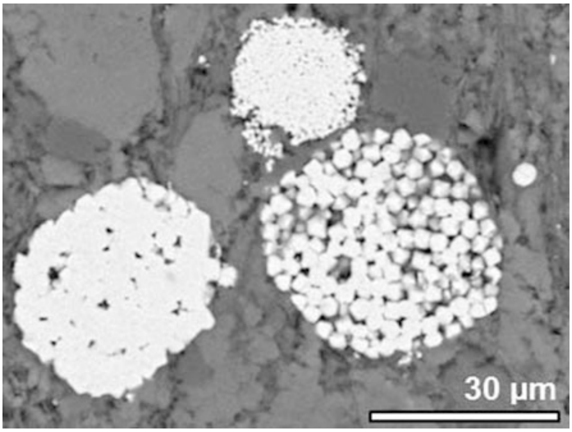
In addition to the sub-cubic, octahedral and vein-type morphologies, pyrite framboids were abundant in all the samples. The framboids were typically found disseminated within the rock but were also common on fracture surfaces. It was observed that the framboids showed a wide variation in each of the following properties:

1. Size (diameter)
2. Large-scale morphology
3. Number of microcrystals and ordering
4. Microcrystal morphology and habit

Framboids in the Baytown samples ranged from <5 μm up to about 40 μm. Other aggregations of octahedra in non-framboidal morphologies were present at larger sizes, up to 60–100 μm across. A common observation was the co-existence of pyrite framboids of various sizes within 10 μm of each other (Fig. 7).

In most cases the pyrite framboids display a near-spherical form, sometimes producing a "poly-framboidal" appearance (Fig. 8). However, there are some instances where the large-scale structure is non-framboidal but still comprises pyrite microcrystals. In these instances, forms include rods (Fig. 9), cubes, octahedra (Fig. 10) and anhedral scattered masses (Fig. 11). Non-spherical types

**Fig. 7** Various pyrite framboid sizes, from <1 μm (far right) to >30 μm. Microcrystals are arranged in a disordered manner with varied orientation



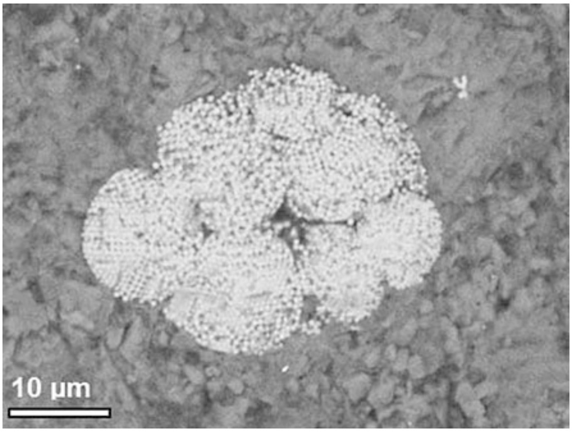


**Fig. 8** Variations in framboid macro-structure and ordering/packing; sub-spherical framboids clustered together producing a "poly-framboidal" appearance

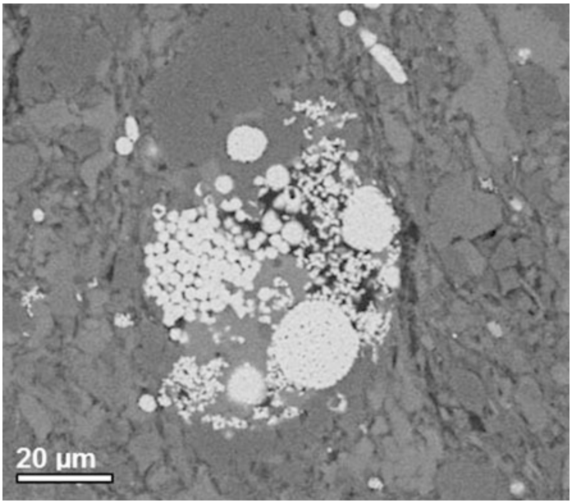


**Fig. 9** Variations in framboid large-scale morphology—spherical clusters (*centre*) and elongate rods (*top-centre*). Dispersed masses of microcrystals are also present

would more appropriately be termed "aggregations" or "clusters" of pyrite microcrystals.

Ohfuji et al. (2005) identified two internal structures for framboids which can be generalised as ordered and disordered. Although examples of both types are seen within the Baytown samples, the disordered form appears to be dominant (e.g., Fig. 7). The Baytown samples also exhibit a wide range of packing densities, which appears to be a function of the orientation, size and habit of the individual microcrystals. In some cases microcrystals appeared aligned into rows whilst in others the microcrystals are scattered widely (Fig. 11).

Variations in microcrystal size directly influence the number of microcrystals possible within a framboid. There are several occurrences of equal-diameter

**Fig. 10** Variations in framboid large-scale morphology—spherical clusters and sub-octahedral aggregations

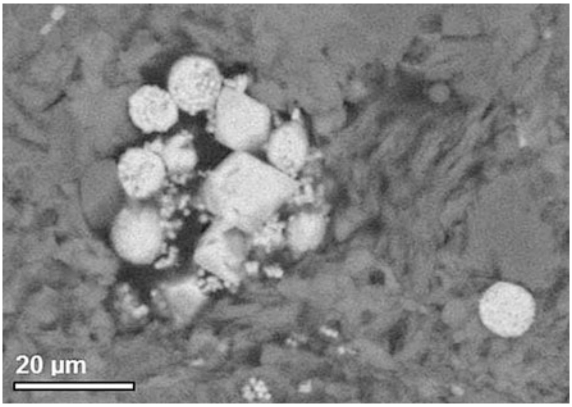
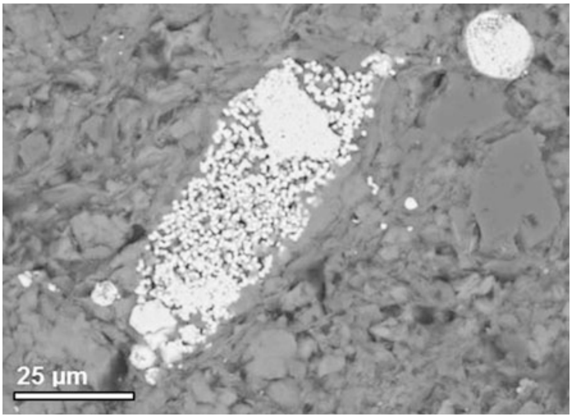


**Fig. 11** Variations in framboid large-scale morphology—anhedral mass of dispersed/scattered pyrite microcrystals. Note cracking in pyrite cube (*bottom-left*)



framboids adjacent to one another but with stark differences in microcrystal size and quantity (e.g., Fig. 7).

Two major types of microcrystal habit were observed within the pyrite framboids. Octahedral microcrystals are by far the most common (Fig. 12), but pyritohedra (irregular dodecahedra) were also observed. In some cases high magnification of the microcrystals revealed that they had a very tightly packed framboidal structure, containing many smaller microcrystals, although the individual habits could not be identified (Fig. 12).

A common texture observed within the samples from Baytown is the fracturing or cracking of microcrystals within framboids (Fig. 13). This microcrystal appearance is not known to have been previously reported in the literature, although several authors have published SEM images of fractured microcrystals without addressing this aspect (e.g., Ohfuji et al. 2005). Cracks vary considerably in their appearance but in general they are observed as irregular or undulating dislocations (Fig. 14). In some cases the fractures traverse an entire microcrystal and may cause it to break into two (Fig. 15).

**Fig. 12** Variations in pyrite microcrystal habit—equant octahedra (*top-right*) and "micro-framboid" or framboidal microcrystal (*left*)

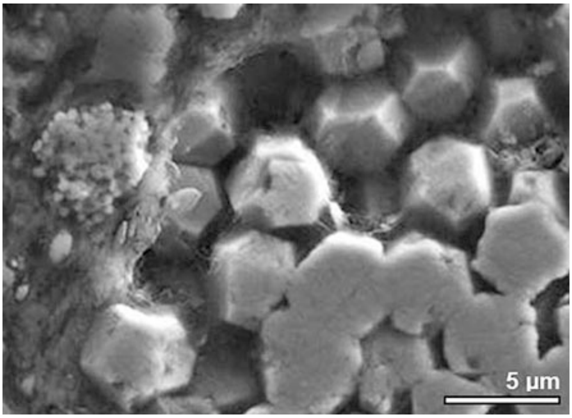


**Fig. 13** Pyrite framboid with microcrystals displaying irregular fractures

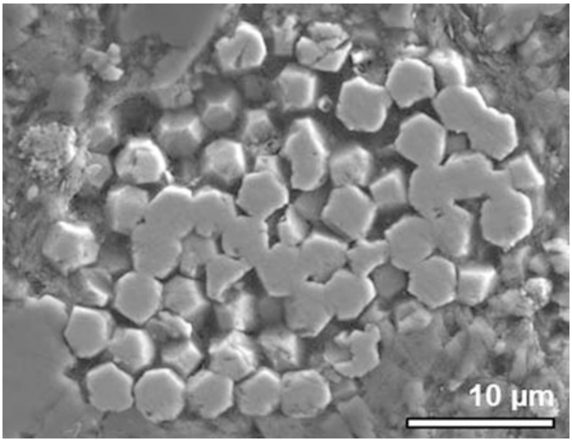
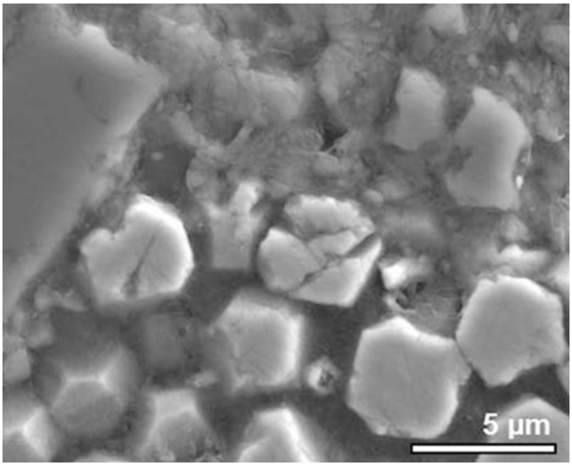


**Fig. 14** High-magnification image of fractured microcrystals



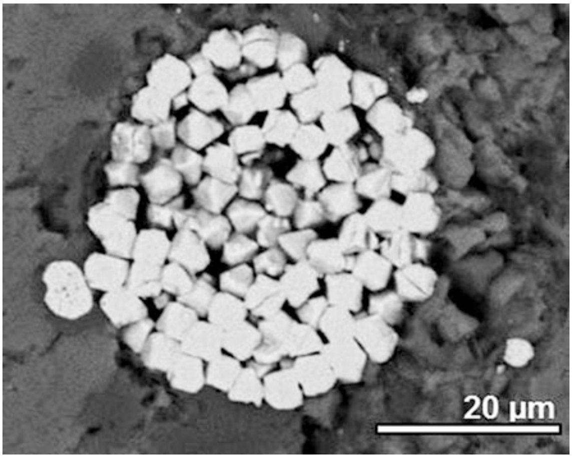


**Fig. 15** Pyrite framboid showing fracturing of over half the microcrystals, many of which are completely divided into two

The cause of the microcrystal cracking is not known at present, but could be related to tectonic shearing or faulting. They are unlikely to be the result of sample preparation as although fine (<0.1 µm) polishing scratches can be seen on some samples, the fractures are typically wider and show a distinctly different, irregular orientation to the scratches. The cause of the cracking is the subject of ongoing research.

## *Implications of Framboid Geometry for Oxidation*

Framboidal pyrite is widely believed to oxidise faster than pyrite in “chunks” or cubes of equal size (e.g., Pugh et al. 1981). The porous nature of the structure, a result of the spacing between individual microcrystals, provides a large exposed surface area on which oxidation reactions can occur.

The differences in framboid morphology and texture observed in the Baytown samples will give rise to a range of available surface-area-to-volume ratios (specific surface). In particular, the fracturing of a single octahedral microcrystal into two identical halves would expose two relatively large new faces, both square in shape. In this scenario, the theoretical surface area for the entire microcrystal would be increased by some 160 %.

Consequently, these varied framboid morphologies and textures will influence the rate of oxidation and thus the release of sulphuric acid/formation of sulphates. In general, framboid characteristics which are likely to promote fast oxidation rates are:

1. Large numbers of microcrystals
2. Small microcrystal sizes
3. Large microcrystal surface areas

4. Low density and high void space
5. Fractured microcrystals

Observations made on the samples of Carboniferous calcareous mudrock from Baytown suggest that whilst the presence of framboidal pyrite can be detrimental to civil engineering, the texture and structure of the framboids will have a significant influence on the rate and severity of any adverse effects.

## Effects of Surface Heating

Ireland is not well known for geothermal energy and has a relatively limited number of such resources (Lund et al. 2011). Despite this, there are at least 42 warm springs recorded in Ireland, with temperatures ranging from 13 to 24.7 °C (Aldwell and Burdon 1980). The potential for geothermal development has been noted in the past (e.g., Aldwell and Burdon 1978) but it was not until 2004 when the Sustainable Energy Authority of Ireland commissioned a study into the nature of ground-sourced heat that it was fully appreciated.

The final report of the CSA Group study (2004) includes a number of geothermal maps based on measured and modelled temperatures at a variety of depths. It also includes a compilation of data and discussion of the Irish thermal springs, which are suggested as possible resources for geothermal exploitation. The findings of the CSA Group report are discussed below with reference to the implications for the sulphate-induced heave process.

### *Irish Thermal Springs*

Warm springs in Ireland can be broadly divided into the Leinster and Munster springs. The Leinster springs are the closest to the Dublin area and hence the Munster springs are not considered here. Thermal springs, wells and boreholes listed by the CSA Group within 50 km of Dublin are plotted in Fig. 16. The temperature of the springs typically ranges from 12 to 25 °C, with temperatures tending to increase with discharge and flow rate. In general, both temperature and discharge peak in the spring and summer months (e.g., Fahy 1975).

It can be seen that all 18 of the springs plotted in Fig. 16 issue from rocks of Carboniferous age, which are typically overlain by a layer of glacial deposits or boulder clay in the east of Ireland. Figure 16 also shows that the North Leinster springs are located sub-parallel to and north of the Blackrock-Rathcoole Fault, an observation discussed by the CSA Group (2004). This fault separates the Carboniferous rocks from older rocks to the south (including the Leinster Granites) and has been postulated as the heat source for the springs. A number of other faults are also recorded on the 1:100,000 geological map apparently radiating from the

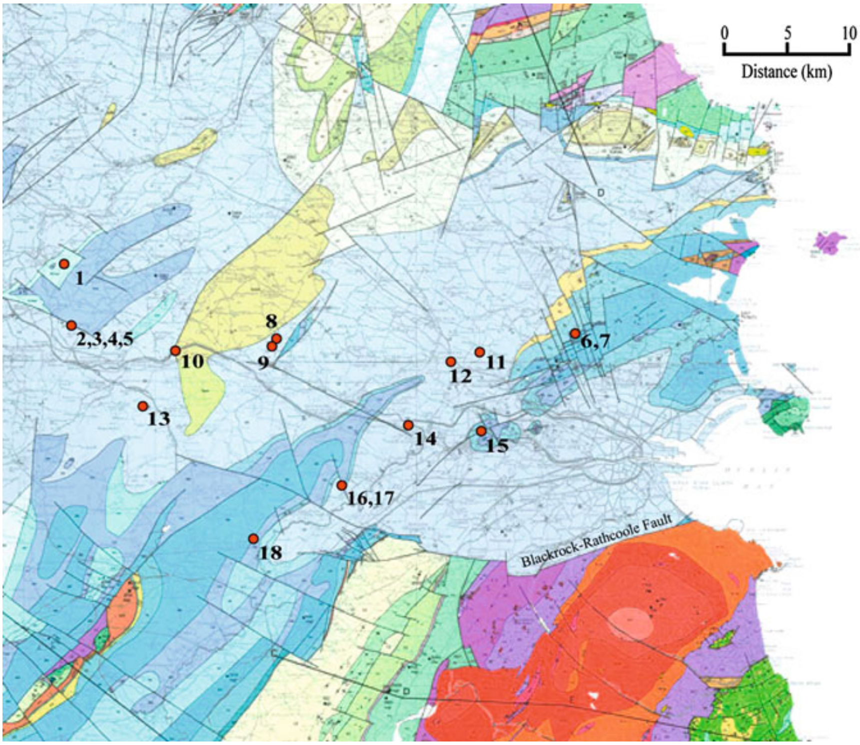


**Fig. 16** Approximate locations (Nos 1–18) of thermal springs, wells and boreholes in the Dublin region. Geological map adapted from GSI (1995; 1999)

Leinster Granites. Undoubtedly there are many less significant faults which are not included on this small scale map. Examination of Fig. 16 reveals that all the springs are close to a mapped fault (i.e., within a few kilometres) and many appear to issue directly on the fault trace.

The spring water itself has been shown to have a meteoric origin, with the exception of locality 14 in Leixlip (CSA Group 2004). It is believed that this meteoric water is circulated within deep fault structures related to the Blackrock-Rathcoole Fault where it becomes heated and later rises to the surface through fracture systems (CSA Group 2004; McConnell et al. 2001).

## *Shallow Heat-Flow in the Dublin Area*

Typical soil temperatures in Ireland range from 9.5 to 12 °C in the uppermost 1.5 m (CSA Group 2004) whilst typical shallow groundwater temperatures are in the range of 10–12 °C (Aldwell 1997). Local temperature anomalies have been identified and were elucidated on a map of contoured heat-flow density for the depth range of 0–100 m which was produced as part of the CSA Report. The map indicates that whilst Northern Ireland hosts warmer sub-surface material than the south, there are several areas which display an above average heat flow density, including the Dublin area.

Surface heat-flow density in the Dublin area modelled by the CSA Group (2004) exceeds 75 mW/m, with heat-flow decreasing away from Dublin (Fig. 17). A local maximum coincides with the area underlain by Caledonian granite in Co. Wicklow. Other Caledonian granites in the east of Ireland include the Kentstown Granite (c. 40 km north west of Dublin) and the Drogheda Granite (c. 45 km north of Dublin). The former is buried at some 500–600 m depth and overlain by Carboniferous strata while the latter was encountered in a shallow excavation (McConnell and Kennan 2002). Jones et al. (2011) report that the Irish granites continue to generate heat despite their Caledonian age and may contribute to the surface heat flow.

Both the thermal springs and the granites locally increase the ground temperature (CSA Group 2004). As a consequence of the warm ground, several buildings in the Dublin area operate ground-source heat pumps, including one installed in 1994 at Temple Bar which utilises a borehole in the Carboniferous strata (O'Connell and Cassidy 2003).

## *Implications for Iron Sulphide Oxidation*

It is well established that elevated temperatures increase both the extent and rate of iron sulphide oxidation (e.g., Quigley and Vogan 1970; Hawkins and Pinches 1987; Hawkins (2013 this book). Lehmann et al. (2000) report the rate of oxidation of pyrrhotite increases by up to four times with a temperature rise from 25 to 40 °C.

Figure 16 indicates extensive faulting in the Dublin Basin, including both a WSW-ENE fault set (sub-parallel to the Blackrock-Rathcoole Fault) and a NW–SE set. Faults play an important role in the movement of groundwater and it is likely that the NW–SE orientated faults provide a pathway for transmission of heat away from the Leinster Granites and across the basin. In view of the difficulty of mapping faults in argillaceous rock, thermal waters may also occur associated with unrecognised fault zones in this area.

Much of the Dublin area is overlain by the Dublin Boulder Clay (DBC), a geologically recent glacial till. The DBC is a stiff, fissured till with a permeability between $10^{-9}$ and $10^{-11}$ m/s, although higher values may be present in granular zones. Long and Menkiti (2007) have shown that where lodgement till is present, it is highly fissured but the discontinuities are tight/closed. Considering the low permeability and closed nature of the fissures, the DBC may act as an insulating "cap" for upwelling thermal fluids in the Dublin area. Particularly to the north of Dublin where the superficial cover is relatively thin, engineering works for foundation construction may remove (or reduce the thickness of) the DBC and expose locally warm sub-surface conditions.

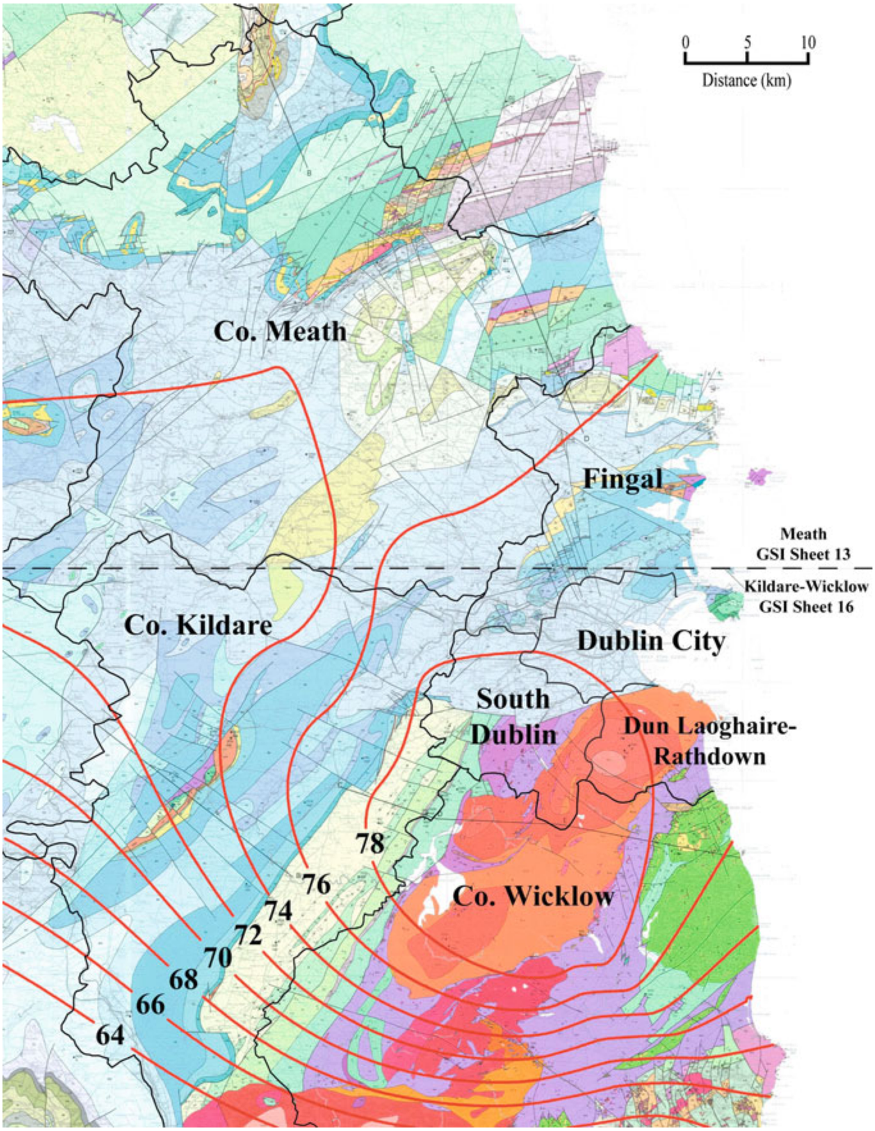


**Fig. 17** Heat-flow density (*units* milliwatts/metre) map of the Dublin area (CSA Group 2004) for depths of 0–100 m, superimposed upon the 1:100,000 regional geology, adapted from GSI maps (1995; 1999)

In cases where sulphide-bearing aggregate or fill has been placed in areas of locally warmer ground conditions, oxidation will occur more rapidly. As a result, the rate of sulphate-induced heave and hence the manifestation of damage in affected structures may be accelerated. The higher temperatures during the spring/summer months may also exacerbate oxidation effects in already naturally warmer ground.

As noted above, soil temperatures in Ireland typically range from 9.5 to 12 °C in the uppermost 1.5 m. Soil temperature data from the Canadian National Climate Data and Information Archive for a weather station in Montréal gives an annual range of 5–7.5 °C for the same depth interval over a 15 year period. These conditions go some way to explaining why damage has typically been manifested in two to three years in Dublin compared with around five to ten years in many Canadian case histories (e.g., Maher 2013).

## Conclusions

This chapter draws attention to some of the ongoing research work being undertaken to better understand the processes of sulphate heave and concrete deterioration in the Dublin area of Ireland. In order to provide a background, examples of problems related to iron sulphide oxidation from other parts of the world are also discussed.

The chapter considers four main topics:

1. The origin and significance of pyrrhotite, which can oxidise some 100 times faster than pyrite. It is considered that to date the presence and significance of this form of iron sulphide has not been adequately appreciated in Ireland.
2. The variable size of the iron sulphide microcrystals (typically between 0.25 and 5 μm); the differing size of the framboids into which they cluster; and the variable degree of packing (from tightly packed/ordered to more open porous disordered structures), all of which have an effect on the speed of oxidation.
3. The fact that microcrystals <5 μm across may be fractured. The examples studied from a specifically drilled rotary-cored borehole indicate that such fractures are not induced during the quarrying process but probably relate to tectonic stresses, hence may be more commonly found in the vicinity of faults. The presence of these fractures greatly increases the available surface area of the microcrystals hence increasing the potential speed of oxidation of pyrite and/or pyrrhotite. It is also noted that cubes/lumps of pyrite are frequently fractured during the quarrying processes hence this form of pyrite should not be considered "non-reactive".
4. The near surface ground temperatures beneath Dublin are higher than would occur over much of Ireland. In addition to the locations where thermal springs are recorded, undoubtedly heat will also rise to the surface via the linear faults and master joints which radiate from the Leinster Granite. The presence of unmapped springs, concealed by developed land, is also possible. Where the overlying Dublin Boulder Clay is thin, engineering works may reduce the thickness of the impermeable cover such that individual house plots on a single estate may have different temperatures at foundation level or in the fill. For this reason the rate of oxidation of iron sulphides and the associated ferrous sulphate-produced heave as well as the growth of gypsum, ettringite and thaumasite may vary widely across a site.

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