

# The Measurable Effects of Pyrite Concentration in the Lucan Formation on Thermal Conductivity and Modeled Geothermal Collector Length

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pyritic syn-genetic halo present within the Lucan formation.

## ABSTRACT

Bedrock thermal conductivity is an important factor controlling the performance of a shallow vertical geothermal systems. This value can be affected by a number of bedrock characteristics such as porosity, mineralogy and structure (Robertson, 1988). The mineralogy of a rock type is one of the more important characteristics in controlling thermal conductivity (Nabawy & Geraud, 2016), (Blazquez et al., 2017). However, the presence of pyrite mineralization in sedimentary carbonates and its effects on thermal conductivity has not previously been researched. This study appears to show that natural variation in the banded syn-genetic framboidal pyrite within the Lucan Formation in Ireland has a measurable effect on the thermal conductivity results obtained using Divided Bar Apparatus (DBA). These variations have enough of an impact to alter geothermal collector design based on EED modelling software. Field observations of bedrock mineralization and future mapping of these syn-genetic halos (Marx, 2018) could help in determining the likely ground conditions for future shallow vertical geothermal projects in the Dublin Basin.

## 1. INTRODUCTION

### 1.1. Study Area

The study area itself could be interpreted as the entire area of the Dublin basin underlain by the Lucan Formation which is approximately 4300 km<sup>2</sup>. Work is currently being carried out in order to better define the hypothesised syngenetic halo that is thought to be present within the Lucan formation. It can be seen in fig 1 that the Lucan formation covers a large part of the area of the east of Ireland known as the Dublin basin. This includes Dublin city as well as many highly populated towns around the Dublin City commuter belt. This study could be of interest to many of the residents or building owners within this zone that may be considering geothermal energy as a resource. The borehole used for the purposes of this study is an exploration drill core located within this

### 1.2. Lucan Formation Geology

The Lucan Formation consists predominantly of thinly bedded laminated dark limestones and shales with ages ranging from Chadian to Asbian (Ashton et al, 1987). This formation has also been referred to as the Calp Formation of the Dublin Basin by the GSI. Ages have been constrained by biostratigraphic markers containing foraminifera and corals (Strogen, Jones & Sommerville, 1990). This formation was found to have a maximum observed thickness of 1123m which was recovered in the "Athboy Borehole" referenced in Strogen, Jones & Sommerville, 1990. These rocks also make up a large portion of the bedrock around the Greater Dublin Area as well as parts of County Meath and Kildare (Fig 1). It is suggested that the formation represents a transgressive period in the Dublin Basin history and contains many deep water shales and turbidite horizons. These turbidite horizons consist of marine calcarenites and sandstones interbedded with fine grained illites and shales (Larcombe, 2015) These rocks are thought to post-date the main mineralization event that formed much of the lead and zinc sulphide ore around Tara Mines (Ashton et al, 1987) as they can be found to directly overlay the ore bearing boulder conglomerate that is thought to be part of a listric slide event (Strogen, Jones & Sommerville, 1990) in the Dublin Basin's history.

### 1.3. Lucan Formation Hydrogeology

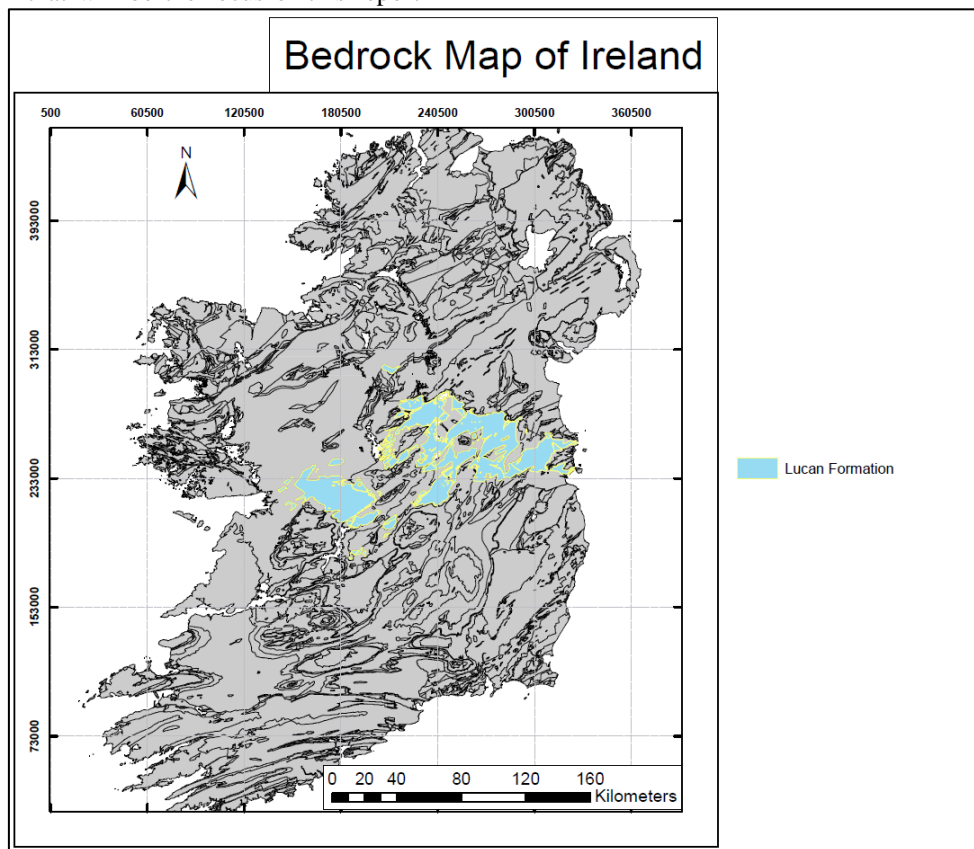
The Lucan Formation is classed as a locally important aquifer and is the main aquifer underlying Dublin City. Much of the area within the Lucan formation is listed as having extreme ground water vulnerability which is particularly problematic in urban centres where industrial processing plants are common place and waste water is likely produced in high volumes. The aquifer itself is termed moderately productive which in the case of geothermal development means that drilled wells are very likely to contain some degree of groundwater.

### 1.4. Lucan formation mineralization

The Lucan Formation also contains potentially significant syn-genetic pyrite mineralization within the

hypothesized syn-genetic halo described by Marx, F., (2017). This pyrite is thought to have formed in a syn-sedimentary environment in a basal marine setting (Anderson et al, 1998). Evidence for this can be seen in the fine grained and banded texture of the pyrite mineralization within core samples. Sulphur isotope analysis also suggests that the sulphur has a strongly bacteriogenic signature consistent with precipitation out of the sea water after combining with iron that was exhaled by sub-marine hydrothermal vents (Fallick et al, 2001). Microscopic analysis of this pyrite also shows fine grained framboidal grains mainly within the argilacious assemblages (Larcombe, 2015). This is in contrast to the high grade ore assemblages of lead and zinc sulphides found in the stratigraphically lower pale beds of the Navan Group and the coarse grained and often complex textures of the mineralization associated with them. (Ashton et al, 1987). It is this fine grained, disseminated, framboidal pyrite mineralization that will be the focus of this report in

which the aim will be to determine if natural variations in pyrite concentration within the Lucan Formation can significantly impact on thermal conductivity. Previous work has been carried out to determine the thermal conductivity of well-formed, crystalline pyrite of 99.5% purity (Popov et al, 2012). The findings of this experiment showed a conductivity value of 47.8 +/- 2.4 W/mK at room temperature that far exceeds thermal conductivity values commonly seen in limestone and shale rocks. However, the pyrite in the Lucan formation is at far lower concentrations than that of the Popov experiments and pyrite abundance is disseminated and contains sulphur of bacteriogenic origin. Crystal structure of the pyrite in the Lucan formation is largely framboidal compared to the euhedral cubes of pyrite tested in the Popov experiments (2012). These factors may prove pivotal in determining the results of the analysis.



**Figure 1: This is a bedrock map of Ireland highlighting the spatial significance of the Lucan Formation across the Country (source GSI).**

## 2. METHOD

### 2.1. Core Sampling

The Lucan Formation was targeted for this study as it is the main formation underlying the most significantly populated area in Ireland. Representing roughly 3800 km<sup>2</sup> of bedrock in the Dublin basin it is thought to directly underlie a population of approximately 1.5 million. An Online resource called the Exploration and Mining Viewer was used to identify boreholes that were drilled within the Lucan Formation. Due to interest in base metal exploration in

the area there was a wealth of data to choose from. This meant that boreholes could afford to be filtered based on their location, recorded pyrite content, date drilled and their availability. The borehole chosen for the purposes of this study was donated by New Boliden Tara Mines and was freshly drilled on the 03/04/2018. This borehole had encountered a thick succession of the Lucan formation with significant visible pyrite banding. A total of 10 samples of core were taken from the borehole, each measuring roughly 300 mm in length. The samples were chosen based on

having a low angle of bedding; low fracture and veining density; similar lithological composition throughout and a visible range in pyrite content throughout. A powdered sample from each length of core was then taken by running an abrasive wheel along the length of the each sample at a uniform depth. These samples were then bagged and given a tag with a randomized sample number relating to the original sample number. Each powdered sample was then sent off to a lab for analysis of total Sulphur and Sulphate. The rest of the core sample was then prepared for thermal conductivity analysis using the divided bar technique.

## 2.2. Pyrite Analysis

Pyrite analysis of the powdered samples was carried out by Nicholls Colton Laboratory in the UK. Total sulphur and acid soluble sulphate was measured in accordance with BS EN 1744. Total pyrite / oxidisable sulphide was calculated using the below formula [1].

$$[(TS) - (AS \times 0.4)] \times 1.87 = OS \quad [1]$$

$TS$  = Total Sulphur  
 $AS$  = Acid Soluble Sulphate  
 $OS$  = Oxidisable Sulphide

The value for oxidisable sulphide was taken as the mass percentage of pyrite in the sample. This value may also comprise of a small percentage of other oxidisable sulphides such as zinc and lead sulphides that are also observed in the banded pyrite mineralization but in far smaller concentrations.

## 2.3. Thermal Conductivity Measurements.

The thermal conductivity of each core sample was calculated by testing four discs from each core sample. Each disc cut represented the overall mineralogy of the core sample while avoiding obvious calcite veining that could impact on thermal conductivity results. The discs were then placed in the Divided Bar Apparatus which would measure unidirectional heat flow in the sample which would allow a value for thermal conductivity based on Fouriers Law to be determined. [2].

$$Qx = -kA \frac{dT}{dx} \quad [2]$$

$Qx$  = Heat Flow in direction  $x$   
 $k$  = Thermal Conductivity  
 $A$  = Cross-sectional Area

$\frac{dT}{dx}$  = Temperature Gradient in direction  $x$

An average thermal conductivity for each sample was then calculated and was taken as the representative value for that section of core. These results were then plotted along with their pyrite content on a scatter plot to determine if there was a correlation between the two values.

## 3. RESULTS

### 3.1. Pyrite Analysis

The chemical analyses of the Lucan Formation powdered samples were carried out by Nicholls Colton Group based in the UK. Their results are in accordance with BS EN 1744. Results for Total Sulphur and Total Sulphate were used to determine the likely concentration of pyrite in each core sample. Table 1 shows the results from this analysis as well as the name given to each core sample in the left most column.

**Table 1: This table shows the results obtained from total sulphur and sulphide analysis carried out by Nicholls Colton Labs.**

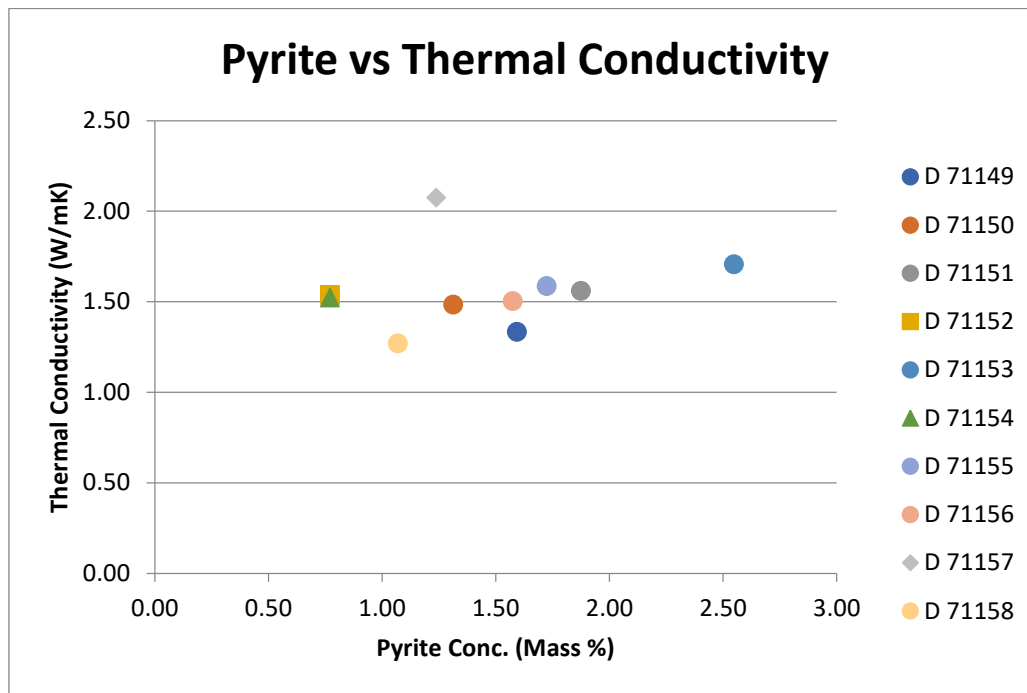
Lab Sample No.	Total S mass %	Total S in Sulphides mass %	Total Pyrite mass %
D 71149	1.1	0.852	1.59
D 71150	0.95	0.702	1.31
D 71151	1.25	1.002	1.87
D 71152	0.66	0.412	0.77
D 71153	1.61	1.362	2.55
D 71154	0.66	0.412	0.77
D 71155	1.17	0.922	1.73
D 71156	1.09	0.842	1.58
D 71157	0.91	0.662	1.24
D 71158	0.82	0.572	1.07

### 3.2. Thermal Conductivity Analysis

Thermal Conductivity tests were carried out on 3 discs per core sample. Discs were selected on their overall optical mineralogy to represent the core sample as accurately as possible. Table 2 records the thermal conductivity values of each disc as well as their average value for each core sample.

**Table 2: Table displaying the thermal conductivity of each disc tested per core sample and average TC value for each core sample.**

Sample No.	Thermal Conductivity W/mK				
	A	B	C	D	Average
D 71149		1.14	1.24	1.62	1.33
D71150	1.4	1.25	1.8		1.48
D 71151	1.37	1.95	1.36		1.56
D 71152	1.32	1.17		2.12	1.54
D 71153	1.72	1.56	1.84		1.71
D 71154	1.32	1.66	1.59		1.52
D 71155	1.26		1.73	1.77	1.59
D 71156	1.57	1.56	1.38		1.50
D 71157	1.77	2.26	2.19		2.07
D 71158	1.02	1.38	1.41		1.27



**Figure 2: This is a graph showing the pyrite content and thermal conductivity of all ten samples from this study. Samples D 71152 and D 71154 that plot furthest left on the graph have a high concentration of coarser grained limestone that was not visible until the sample dried. Sample D 71157 was prepared under different conditions to the other nine samples and therefore should be considered separate from the other samples.**

## 4. DISCUSSION

### 4.1. Pyrite and Thermal Conductivity

Thermal Conductivity results of the sampled Lucan Formation drill core show a potentially significant correlation with syn-genetic pyrite concentration. Mineralogy and changes in sampling procedures aside, this report has shown that with natural increases in pyrite concentration, an increase in thermal conductivity can also be observed. This could have substantial implications in the design of geothermal collector systems in the future around inner city Dublin and the surrounding commuter belt. Pyrite has already been proven as a relatively good thermal conductor at room temperature by previous attempts to measure the thermal conductivity of solid and relatively pure crystals. Two crystals tested in the experiments performed by Popov et al, (2012) yielded thermal conductivity results similar to crystal semi-conductors. It would therefore be logical to assume that thermal conductivity in shales should be improved by the presence of pyrite, however, it was not known how significant or measurable this improvement might be. The results from this report show that pyrite concentrations varying in as little as 1.1% of total rock mass could influence thermal conductivity by a degree of 0.44 W/mK. These numbers become far more significant the larger the geothermal collector design. The Lucan Formation underlies a large portion of the population of Ireland as well as many urban centres making it a far more likely target than many other geological formations in Ireland to be exploited for

geothermal energy. This means that large geothermal collector systems could benefit from the results of this study. Small changes in the overall thermal conductivity of the bedrock can affect the collector length required for a building with specific heating requirements. The larger these requirements, the longer the collector length needs to be and the greater the effect that variations in thermal conductivity will have on the overall design.

### 4.2. Collector Design

The overall design of a geothermal collector is influenced by a number of key factors including ground conditions, the type and size of the ground source heat pump being used and the peak load and running time required of the system. Thermal conductivity is one of the parameters included in these ground conditions. Modelling software such as Earth Energy Designer, allow the user to input values manually depending on either lab analysis of the bedrock or estimated values for thermal conductivity. It was considered important that, as part of this report, a practical example explaining the importance of thermal conductivity be included in the overall study. Figure 3 from work published by the IGTP (Pasquali, 2015) shows the impact that ground conditions can play in determining geothermal collector design. This table was published to act as a guide for installers of geothermal systems and promote proper installation practices for these systems in order to limit future issues and try to rebrand the technology as an effective

way to save energy. Poor installation has previously damaged the reputation of geothermal collectors due to misinformation regarding the sizing requirements of each system. This table also shows the impact that small changes in thermal conductivity can have of the collector length of a system.

In order to show the impact that thermal conductivity variations in shale will have on collector length, a number of assumptions will have to be made in order to correctly model a geothermal collector design.

- 1) The Lucan Formation is strongly interbedded with tight limestones and shales. Based on field observations taken by Geoserv from Dublin city (2018); the shale to limestone ratio is roughly 50:50.
- 2) Ground water temperatures will be taken at 11 degrees Celsius.
- 3) Based on results obtained by the USGS report on thermal properties of rocks (1987), limestone with low porosity is thought to have a thermal conductivity value averaging about 2.5 W/mK.
- 4) The heat pump used in the modelling of the above table is a small residential scale heat pump with a capacity of 10 kW.

In this report, sample D71158 had the lowest value for thermal conductivity measured in the Lucan formation

shale samples and coincided with the lowest value in pyrite concentration. This average thermal conductivity was measured at 1.27 W/mK. With a 10kw heat pump extracting heat from an interbedded limestone and shale with average bulk thermal conductivity of 1.9 W/mK, the recommended collector length would be roughly 312 m of 40mm OD single-u pipe. However if we take the highest value of thermal conductivity for pyrite rich shale from this report, which was 1.7 W/mK and coincided with the largest measured pyrite content of all the samples, the same lithology and heat pump would require just 294 m of collector. Although this difference of 18 m may not seem substantial on the residential scale, larger scale systems could potentially see a far greater difference in collector length where multiple collectors might be installed for the heating of office blocks or for use in industrial applications. It should also be noted that all the thermal conductivity results in this report account for some degree of pyrite content, which means that the thermal conductivity of shales with no detectable pyrite content may in fact exhibit even lower thermal conductivity values. This may be the case for parts of the Lucan Formation outside of areas with significant mineralization.

	1,200 FLEQ hours	Average Peak Extraction Rate (W/m)							
	Average Ground T (°C)	14	13	12	11	10	9	8	7
Thermal Conductivity (W/mK)	4	59	55	52	49	46	43	40	37
	3.8	57	54	51	48	45	42	39	36
	3.6	55	52	49	46	44	40	38	35
	3.4	54	51	48	45	42	39	36	34
	3.2	52	49	46	43	41	38	35	33
	3	50	47	44	42	39	37	34	31
	2.8	48	45	43	40	38	35	33	30
	2.6	46	43	41	38	36	34	31	29
	2.4	43	41	39	37	34	32	30	28
	2.2	41	39	37	35	33	30	28	26
	2	39	37	35	33	31	29	27	25
	1.8	36	34	32	31	29	27	25	24
	1.6	33	32	30	28	27	25	24	22
	1.4	31	29	28	26	25	23	22	21
	1.2	28	26	25	24	23	21	20	19
	1	25	24	23	21	20	19	18	17

**Figure 3: This is a geothermal collector sizing chart from the IGTP project carried out in partnership with SEAI and Geoserv Solutions. This table is for a 10kW heat pump working for a total of 100 hours per annum.**

**5. CONCLUSIONS**

The results found in this report appear to show evidence for a direct correlation between natural syngenetic pyrite concentrations in carbonates and thermal conductivity values obtained using the divided bar method. This was the main aim of this report while also trying to determine if the difference in measured thermal conductivity in the samples containing

varying levels of pyrite was enough to impact collector design. Based on results from thermal conductivity tests it would appear that the presence of thermally conductive pyrite in concentrations ranging from 1 – 2.5% of the overall rock mass is enough to impact thermal conductivity results and collector design. A 10 kW heat pump operating at peak load for 25 years would require a collector length of

approximately 312 m of single-u 40 mm OD pipe if bulk bedrock thermal conductivity is in the lower range of 1.9 W/mK. This is compared to a collector length of 294 m with the same sized heat pump, peak load and limestone shale ratios but with shale thermal conductivity values of 1.7 W/mK instead of 1.3 W/mK and raising the bulk thermal conductivity to 2.1 W/mK. This appears to show that pyrite concentrations can indeed substantially impact the thermal conductivity enough to influence geothermal collector design. In the absence of lab analysis due to a lack of facilities or time constraints, field observations of mineralization and future mapping of these syn-genetic halos (Marx, F., 2017) could help in determining sub-surface thermal conductivity.

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