A STUDY OF THE THERMOLUMINESCENCE OF FLUORITES FROM THE PENNINE OREFIELDS OF ENGLAND

by

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Summary

Four main types of thermoluminescence in fluorite samples from the Pennine orefields, have been determined. The glow-curve produced by calculation can be qualitatively related to the abundance of certain trace elements. The studies show that yttrium is an important factor in classifying the thermoluminescence of the fluorites.

Introduction

The Pennine orefields of England (text-fig.1) typified by deposits of galena, zinc blende, barite and fluorite are similar to others found in North America, Europe, Russia and North Africa, together they represent a remarkable concentration of lead, zinc, barium and fluorine in the Earth's crust. The deposits can be broadly described as stratabound, that is, they are confined to particular stratigraphical horizons on a regional scale but may be discordant on a local scale.

The Pennine orefields have had a long mining history dating from pre-Roman times. Roman pigs of lead have been found in Yorkshire and Derbyshire, together with some old workings thought to belong to this period. Mining, sporadically continued through the Middle Ages, but the main period of lead mining occurred between the late 18th and early 19th centuries. The industry evolved from largely hand-won methods of ore extraction to some degree of mechanisation during the period of the Industrial Revolution.

Lead mining in the Pennines generally ceased in the 1880's with the sharp worldwide fall in the price of lead. Exceptionally, individual mines such as the Millclose Mine (Trail 1939) continued production. An excellent historical review of lead mining history in the Pennines is given by Raistrick and Jennings (1965). More detailed historical accounts of the Alston and Askrigg orefields are given by Dunham (1948: 1974) and by Ford and Rieuwerts (1968) for Derbyshire. Most of the present day mining industry is restricted to the gangue minerals, fluorite and barite, which has grown steadily in importance since about 1900 (Dunham 1944; Notholt and Highley 1971; Collins 1972).

The mineral deposits are associated with Carboniferous limestones and sandstones and shales of Viséan and Namurian age. Igneous activity during the Carboniferous produced the basalt lavas (or toadstones) and intrusives in Derbyshire (Shirley 1949; 1959) and the quartz-dolerite Whin Sill in the Alston orefield (Dunham 1948). Stratigraphy played an important role in localizing the mineralization in a number of preferred rock formations or 'bearing beds'. Each bed is formed into a trap for the mineralizing fluid with an impermeable shale or igneous rock member acting as a cap or floor.

The Pennine orefields are located in tectonically stable upland areas within the Peak District and Yorkshire Dales National Parks. The Northern Pennine orefields rest on Lower Palaeozoic strata, which were initially thought to form a single rigid block (Marr 1921), the latter was subsequently divided into a northern, Alston Block (Trotter and Hollingworth 1928) and a southern, Askrigg Block (Hudson 1933). Geographically, the two blocks are separated by a shallow, broad structural depression including Stainmore and Cotherstone Moor (Versey

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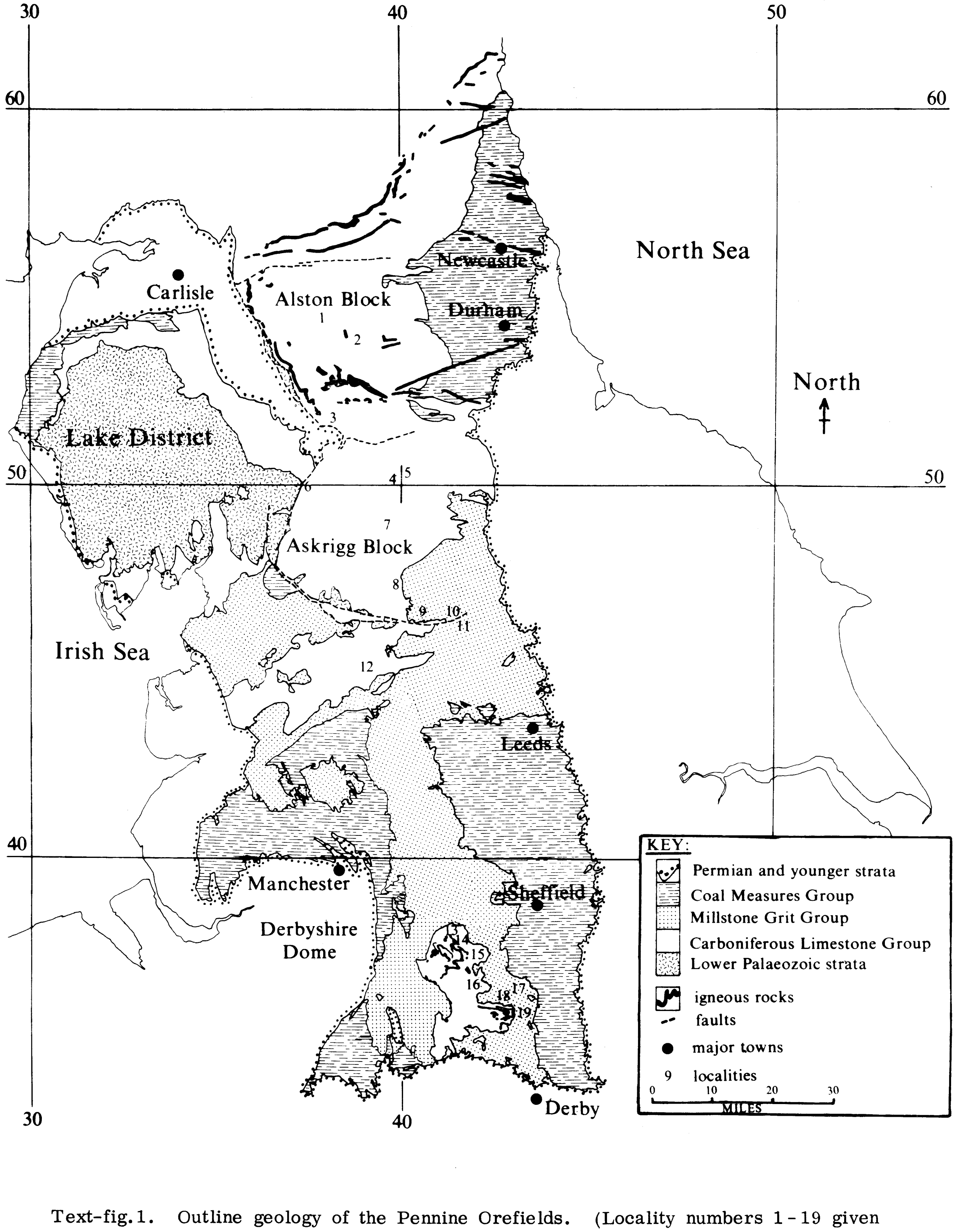
pp.271-280, 4 text-figs.



Text-fig.1. Outline geology of the Pennine Orefields. (Locality numbers 1 - 19 given at the foot of the opposite page).

1927; Reading 1957). Unlike the Derbyshire 'Dome' (Shirley and Horsfield 1940) these blocks are underlain by Caledonian granitic batholiths (Bott 1967) not necessarily concerned with the mineralisation upon which Carboniferous strata lie unconformably (Dunham *et al.* 1965; Dunham 1975). Sedimentation on the blocks during the Lower Carboniferous was generally slow with shallow water deposits accumulating. The intervening gulfs (or basins) of deeper water sediments have up to three times the sedimentary thicknesses of the blocks (Kent 1966, 1974; Dunham 1973).

The main veins occupy mineralized faults usually with a small throw. In the more competent 'bearing beds', these fissure deposits (or rakes) usually form steep ribbon bodies with their length many times their height. Flats (of flots) take the form of bedding-controlled replacement deposits. Pipe deposits normally consist of irregular mineral bodies usually found at the intersection of a fissure or joint and the bedding (Ford 1969). The veins are often found with a banded mineral fill and, despite the generally simple major mineral assemblage, a large number of minor mineral species are found (Dunham 1948, 1959; Ford and Sarjeant 1964). The mineralization is generally polyphase in character often with a complex paragenetic sequence (Ineson and AlKufaishi 1970). Zoning of the gangue minerals is conspicuous in the Alston and Askrigg Blocks (Dunham 1934 and 1952). The zoning of the Derbyshire orefield is discussed by Firman and Bagshaw (1974).

Estimates of the age of the Pennine mineralization vary from Variscan (Moorbath 1962), although this age is disputed (Mitchell and Krouse 1971), to Mesozoic (Dunham *et al.* 1968). Isotopic dating of clay minerals from Derbyshire (Ineson and Mitchell, 1973) indicates a series of mineralizing episodes spread over a 100 million years from Permo-Triassic to Jurassic times.

Previous Analytical Work

Pennine fluorites have been studied using XRF and other methods and analytical results are given by Dunham (1952), Palache *et al.* (1951), Haber Schausberger and Schroll (1967), Derré (1972) and Jeffrey (1967). Smith (1974a) in a very detailed study gives a large number of analyses and demonstrates their application to economic geology (Smith, 1974b). Derbyshire Blue John has been studied in great analytical detail by Mackenzie and Green (1971) and Braithwaite *et al.* (1973).

Thermoluminescence Studies

Thermoluminescence (TL) is the luminescence produced on heating a mineral specimen. The thermal energy dislodges electrons which have been excited and trapped in the crystal lattice by ionising radiation. The electrons drop to the ground state via a luminescent centre and in doing so emit light, which can be measured to produce the glow-curve. TL is therefore a function of the ionising radiation received and the thermal history of the specimen (Randall and Wilkins, 1945).

List of Localities for Text-fig. 1

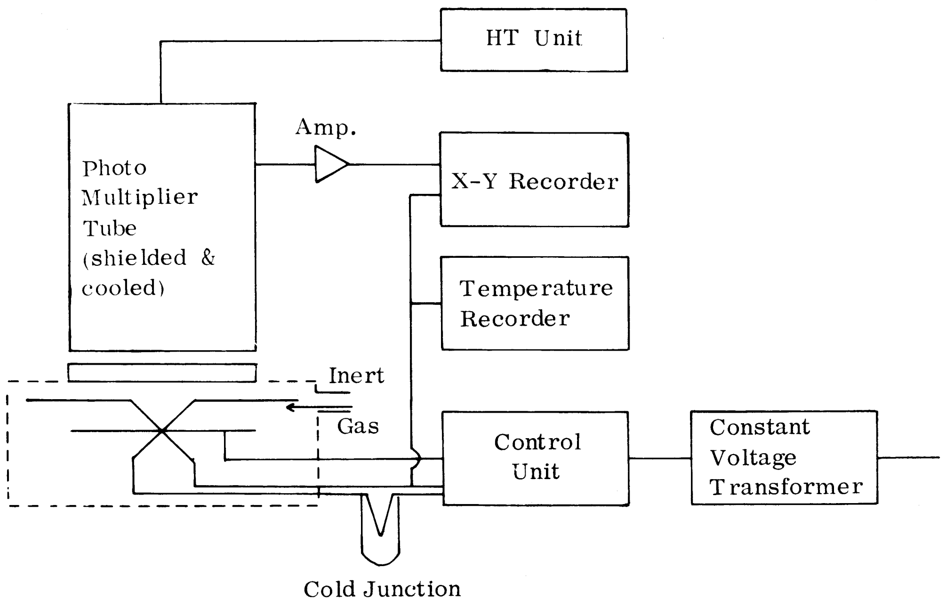
1. Nenthead, Alston Block
2. Weardale, Alston Block
3. Hilton Mine, Scordale, Cumbria
4. Gunnerside Gill, Askrigg Block
5. Arkengarthdale, Askrigg Block
6. Clouds End Fell, Askrigg Block
7. Wet Grooves/Seata Mines, Askrigg Block
8. Kettlewell, Askrigg Block
9. Grassington Moor, Askrigg Block
10. Ashfoldside Beck, Askrigg Block
11. Greenhow Hill, Askrigg Block
12. Raydale, Lothersdale
13. Castleton, Derbyshire
14. Bradwell/Hucklow Edge area, Derbyshire
15. Longstone Edge, Derbyshire
16. Alport mines, Derbyshire
17. Ashover, Derbyshire
18. Matlock area, Derbyshire
19. Crich, Derbyshire

The X-Ray Fluorescence (XRF) method produces secondary x-rays which result from disturbances in the electronic structure by bombarding the specimen with x-rays. The minerals produce unique spectral lines, which, when compared to those of a known standard, enable the chemical composition of the mineral being analysed to be elucidated (Adler 1966). The fluorite lines can then be eliminating leaving the lines of the impurities, particularly the trace elements.

The thermoluminescence (TL) and trace element content of 53 fluorites from the epigenetic mineral deposits of the Pennine orefields have been examined in an attempt to understand the causes of TL and to demonstrate differences in TL between the fluorite samples.

Apparatus and Technique

The apparatus consists (text-fig. 2) of a molybdenum strip heated electrically by an electronic control unit at $5.0 \pm 0.05°C\ s^{-1}$. The powdered fluorite is ground, sieved and placed on a defined area of the filament and heated in an inert atmosphere. The light is measured with an EMI 9635B photomultiplier tube and the amplified signal plotted on the y-axis of an x-y recorder. Temperature, as measured by a chromel-alumel thermocouple, is plotted on the x-axis. A glow-curve is thereby obtained directly, the reproductibility being better than 5%. Samples are "drained" of their natural TL by being heated to 500°C and given a standard dose of about 50 krad of γ-rays from a Co^{60} source. The XRF analyses were performed on a Phillips PW212 machine using synthetic spiked standards of pure calcium fluoride. The detection limits are strontium 2 ppm, barium 8 ppm, cerium 9 ppm, yttrium 3 ppm and lanthanum 5 ppm.



Text. fig. 2. Schematic diagram of the thermolumescence apparatus (from Sears and Mills 1974)

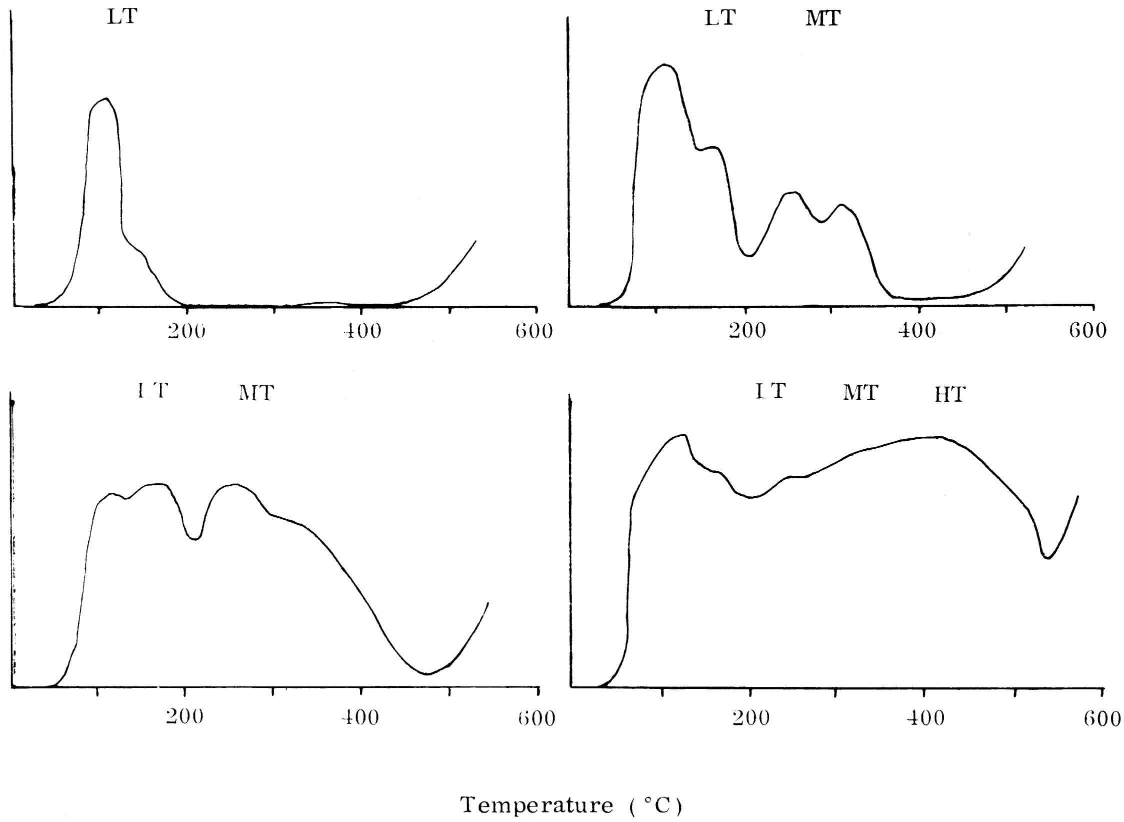
Results

The glow-curves (TL vs. temperature) of the 53 specimens show considerable variation in their structure and in total TL. It was found that distinctive features in the glow-curve can be related qualitatively to the abundance of certain trace elements.

The fluorites and their localities are listed in Table 1 (p. 275). On the basis of their glow curves, the specimens can be divided into four broad groups (text-fig. 3), but there is not always a sharp distinction and some groups grade into each other (for example 2 and 3);

Table 1 - Trace element contents and thermoluminescence of fluorites

Location Fluorite samples	Trace Element Content ppm					Thermoluminescence	
	Ba	Sr	Yr	Ce	La	Area under glow curve (arb units)	Glow curve type see fig. 1.
Escoe Hill, nr. Linton, Yorks.	37	40	19	18	1	386	1
Rimington Mine, Ings Beck, Lancs.	5586	134	23	0	0	978	2
Main Vein, Raygill Quarry, Yorks.	241	39	13	5	9	2317	4
Cloud End Fell, Cumberland.	2845	52	27	0	0	799	3
Birkett Hill, Cumberland.	20	36	24	24	0	381	1
Beevor Mine, Yarnbury, Grassington, Yorks.	13455	143	31	0	0	1690	3
Middle Vein, Grassington Moor, Yorks.	648	53	26	6	14	378	1
Bycliffe Vein, " " "	48	31	27	15	0	494	1
Bycliffe Vein, Ashfoldsidebeck, Yorks.	0	50	81	0	0	881	2
Starbotton Fell, Kettlewell, Yorks.	22	34	21	33	9	424	1
Middlesmoor Pasture "	14506	132	26	0	0	242	1
Galloway Vein, Greenhow Hill, Yorks.	81	44	21	17	5	829	2
Greenhow Rake, " " "	17	47	27	21	0	484	1
Waterhole Veins, Gillfields Adit, Greenhow, Yorks.	24	45	29	26	15	750	2
Lolly Mine, Ramsgill, Nidderdale, Yorks.	269	48	50	21	2	770	2
Inman Vein, Appletreewick, Yorks.	29	38	16	20	3	392	1
Gill Heads Vein, " "	46	48	22	29	3	601	1
Seata Mine, Aysgarth, Yorks.	0	33	28	25	0	1565	3
Wet Grooves Mine, Askrigg, Yorks.	23	46	37	34	0	587	2
Keld Heads Vein, Wensley, Yorks.	2592	58	34	0	0	1842	3
Worton Mine, Nr. Bainbridge, Yorks.	25	46	82	41	5	1609	3
Sir Francis Mine, Nr. Gunnerside Gill, Yorks.	21168	320	47	0	19	1645	3
Bunton Level " " " "	3795	66	60	0	0	1162	3
North Rake Hush, " " " "	14186	160	71	0	0	1993	3
Merryfield Mine, Old Rake, Nr. Gunnerside Gill, Yorks.	5087	75	53	0	4	2415	3
Blakeside Vein, Surrender Moss, Nr. Reeth, Yorks.	5452	119	37	0	0	1163	3
Dam Rigg Vein, Arkengarthdale, " " Yorks.	168	51	49	26	0	583	2
Copperthwaite Vein, " " " "	31688	119	53	0	4	1518	3
Black Hills Hush, " " " "	45	52	45	0	0	1593	3
Moulds Top Mine " " " "	3608	79	47	0	0	1235	3
Blue John, One Vein, Winnats Pass, nr. Castleton, Derbyshire.	29	100	56	28	7	3054	4
Forest Shaft, Odin Vein, Nr. Castleton, Derbys.	13818	214	13	0	0	325	2
Earl Rake, Bradwell, Derbyshire.	13	57	16	31	0	72	2
Dirtlow Rake, Castleton, Derbyshire.	33	39	10	24	0	430	2
Ladywash Mine, Hucklow Edge Vein, Eyam, Derbys	50	48	12	4	1	393	2
Blyth Mine, Alport, Derbyshire.	19	41	16	6	0	130	2
Hazlebadge Hall, Bradwell, Derbyshire.	5071	87	19	0	0	169	2
Gregory Mine, Ashover, "	27	50	11	22	12	275	2
Starr's Wood, " "	3065	126	14	0	3	331	2
Long Rake, Raper Lodge, Alport, Derbyshire.	20778	423	16	0	0	174	2
Old End Mine, Crich, Derbyshire.	88	58	13	26	0	155	2
Clayton adit, Ecton Hill, Staffordshire.	204	37	23	0	2	212	2
Sallet Hole adit, Longstone Edge, Derbyshire.	2818	371	18	0	0	295	2
Low Mine, Great Rake, Matlock, Derbyshire.	20	102	19	43	4	2155	3
Heights Veins, Heights Quarry, Co. Durham.	15	50	293	155	101	3211	4
Knopley Level, Diana Vein, Allenheads Mine, Co. Durham.	95	19	213	63	12	3140	4
Smallcleugh Mine, Nenthead, Northumberland.	0	42	344	108	57	3068	4
Blackdene Mine, Blackdene, Co. Durham.	337	45	31	20	8	2935	4
Redburn Mine, Red Vein, Weardale, Co. Durham.	14	22	316	58	19	3011	4
Whitecheaps Mine, Poor Vein, Blanchland "	20	25	333	77	21	3230	4
Burtree Pasture Mine, Red Vein, Weardale,	17	18	261	52	12	2952	4
Sedling Mine, Sedling Vein, Weardale "	31	27	285	55	26	2885	4
Hilton Mine, Hilton, Cumberland.	47	47	200	49	30	1953	3

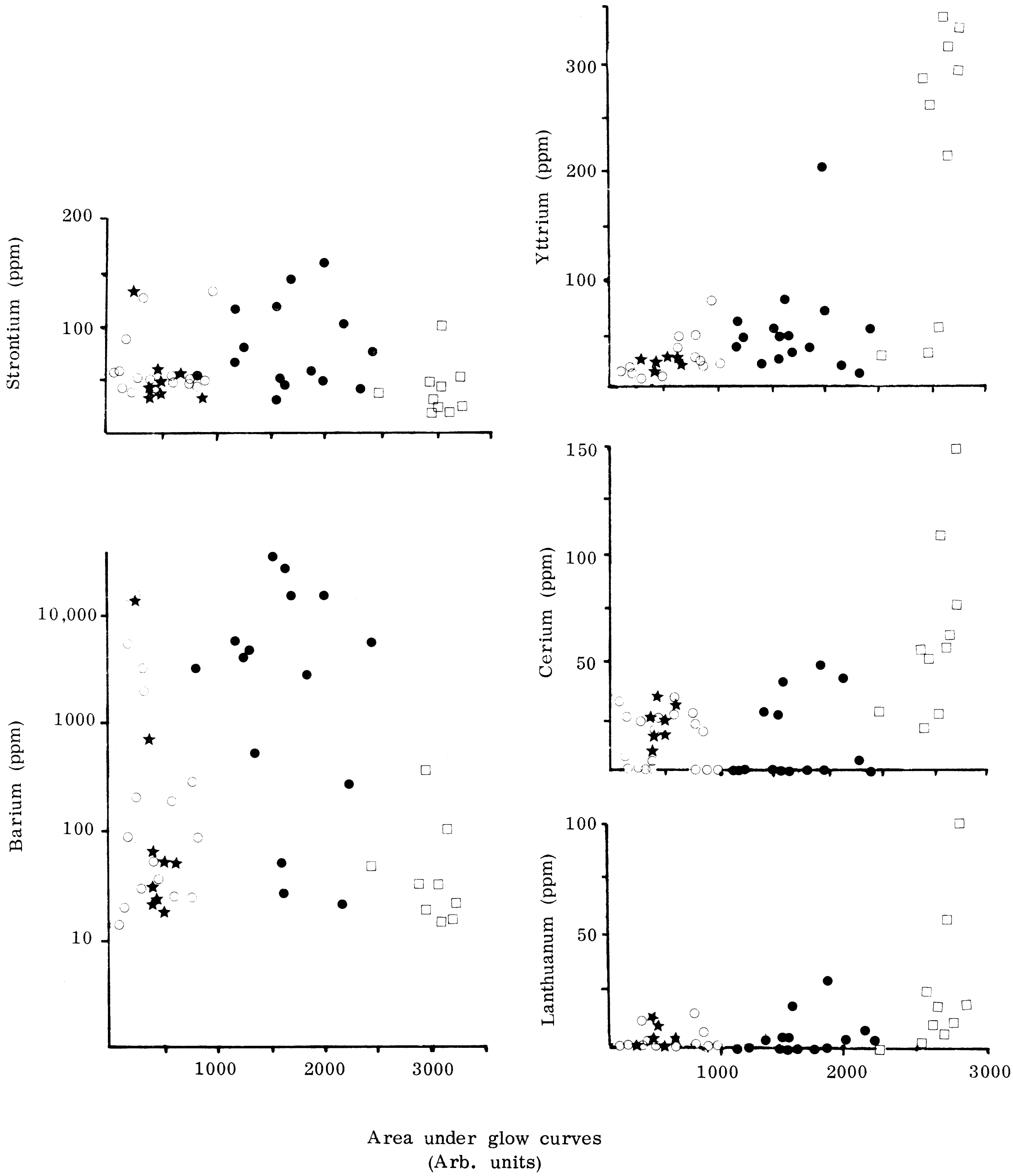


Text-fig. 3. Examples of the four types of glow-curve observed in the Pennine fluorites examined here where the light emitted is measured in the same arbitrary units for each curve. The temperature ranges LT, MT and HT indicate regions in which peaks were observed to appear in the 53 fluorites examined.

some subjectivity is therefore involved in the assignment. Single isolated peaks are rare in the glow-curves obtained but from an examination of all the 53 specimens, peaks appear to occur at $105 \pm 10°$ (this group referred to as LT) 130 ± 15, $165 \pm 10°C$ (referred to as MT), 375 ± 15 and 380 - 450°C (referred to as HT). Some caution must be taken in using peak position values as many factors (especially overlap) change them and the use of the less precise terms LT, MT and HT is preferred. With this nomenclature, glow-curves of type 1 consist only of LT, type 2 of intense LT and some MT, type 3 of intense LT and MT and type 4 of intense LT and HT.

It was possible to measure the content of barium, strontium, yttrium, cerium and lanthanum in all 53 specimens by x-ray fluorescence (XRF). The variation of the TL with trace element abundance is presented in text-fig. 4 in which the various glow-curve types are presented by different symbols. Strontium and barium are assumed to be present in samples of types 1, 2 and 4 in about equal amounts. The remaining glow-curve group, with intense MT, however, contains considerably more of these elements. The barium plot is logarithmic and certain samples with type 3 glow-curves contain more than 1000 times the quantity of barium found in the other types; this is probably due to barite contamination as intergrowths with fluorite.

A few points indicate that some specimens producing type 2 glow-curves contain high barium, but these are clearly separate from the main group of points for this type and are border-line specimens in their glow-curve group assignment. Although some type 1 and some type 3 specimens have barium and strontium, undoubtedly *most* of type 3 have high barium and strontium. Thus an enrichment in elements in calcium-substitutional sites may be responsible



Text-fig. 4. Variation in the content of five trace elements and TL content. The symbols represent the type of glow-curve displayed by the specimens; open circles - type 1, stars - type 2, dots - type 3 and squares - type 4.

for the thermoluminescence in the MT region of the glow-curves of fluorites. The enrichment is analogous to the mechanism for the production of TL in limestones and the feldspars of lunar rocks where manganese substitution for calcium is thought to be responsible (Medlin 1966). The process is contrary to the view (Semec and McDougall, 1969) that TL in this region is associated with Frenkel defects, i.e. interstitial ion-vacancy pairs.

Yttrium and other rare earths, cerium and lanthanum show a quite different trend. These elements, particularly yttrium, are present in greater quantities in samples giving type 4 glow-curves. An association between yttrium, the rare earths and thermoluminescence was mentioned by Menon (1971), and this work supports the conclusion that HT is associated with an enrichment of these elements.

The results do not indicate a relationship between LT glow-curves and trace elements; this supports McDougall (1970) who has suggested that lattice dislocations are responsible for thermoluminescence in this region.

Conclusions

Diagnostic qualitative features of the thermoluminescence (TL) glow-curve of Pennine fluorites can be related to the abundance of certain trace elements. It is possible to distinguish 4 types of TL in the fluorites, although the distinction is not always clear because some types grade from one class into another.

The studies show that the yttrium content is especially important with regard to the HT of Pennine fluorites. HT is a good indicator for the presence of ytrrium and rare earths. The TL also reflects the differences in yttrium and rare earth content between the Pennine orefields, the Alston Block having largely type 4, HT fluorites. The other orefields have a mixture of types 2 and 3 with subordinate type 1. This could well have some significance with regard to the genesis of the Pennine mineralization.

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