

# Metallogenetic significance of a North Pennine springwater

D. A. C. MANNING

Department of Geology, the University, Manchester M13 9PL

AND

D. W. STRUTT

Weardale Minerals Ltd., Blackdene Mine, Bishop Auckland DL14 1EG

## Abstract

The occurrence is reported of a saline spring water from Weardale, which compositionally closely resembles other saline waters derived from the Carnmenellis granite, southwest England. The total dissolved solutes achieve approximately 38000 mg/L, and alkali geothermometers suggest equilibration temperatures of approximately 150°C, equivalent to a depth of 4 km. Using Na, K and Li it is possible to compare the composition of the spring water with those of other spring waters derived from Carboniferous sequences adjacent to the North Pennine Orefield and with published data for fluid inclusions from North Pennine fluorite. These compositional parameters suggest that the ancient mineralizing fluids resemble modern Carboniferous sediment-derived waters and contain a relatively minor component of granite-derived water. Data for Br and Cl indicate that a significant component of the present day Weardale spring waters was probably ultimately derived from organic-rich sedimentary sequences while data for K, Na and Li indicate the importance of a component derived from a permeable granite aquifer. The Weardale springwaters continue to have 'mineralizing' potential, in view of the possibility that they may have precipitated quartz or chalcedony during their ascent.

**KEYWORDS:** spring water, saline water, metallogenesis, North Pennines, England.

## Introduction

THE North Pennine orefield is of considerable historical importance as a major Pb–Zn–fluorite mineralized province, studies of which have shaped concepts of ore formation in similar environments worldwide. Several reviews of the orefield have been published, the most recent of which are those by Dunham (1983), Dunham and Wilson (1985) and Brown *et al.* (1987) which give summaries of the regional geology. Despite a long history of study, the origin of the fluids responsible for mineralization is still poorly understood, although it is generally held that a major component was derived from Carboniferous basins marginal to the mineralized 'blocks'. The purpose of this paper is to report the occurrence of a saline springwater from within the North Pennine orefield, and to contribute to the discussion of the origin of the ore fluids by comparison of data for spring waters from the south west England orefield and Carboniferous sequences within or adjacent to the Pennines with data for North Pennine spring waters and fluid inclusions.

## The Weardale springwater

The spring water reported in this paper was sampled from the Slitt vein within Cambokeels fluorite mine (national grid reference NY 935 383) at a level of 100 m OD. At this level, the Slitt vein passes through dolerite of the Whin Sill, and is approximately 80 m above the roof of the Weardale Granite. Full geological details are provided by Dunham (in press). The Slitt vein is the longest single vein (20 km) in the orefield, and occupies a locally highly permeable fracture system which strikes 060–090°, downthrowing approximately 10 m to the north at this locality (Dunham, 1949).

In addition to the Weardale springwater, samples were taken for comparative purposes from springs at Gilsland Spa (NY 635 678) and Haydon Spa (NY 860 649). These were originally taken as representative examples of brines derived from Carboniferous sequences within the Northumberland Trough; they are incidentally situated close to baryte mineralization along the northern margin of the Alston block. Both springs are sulphurous, issuing onto the banks of the rivers Irthing and Tyne respectively. The spa water sampled at Gilsland is from one of a number of springs derived from the Upper Border Group (Asbian;

Table 1. Compositions of North Pennine spring waters.

sampled	Weardale		Gilsland Spa			Haydon Spa				
	1988	1989a	1989b	1988	3/89	3/89 acidified	10/87	1/88	3/89	3/89 acidified
Li	70.5	42.0	40.3	0.15	0.14	0.14	0.09	0.09	0.11	0.11
Na	7345	3511	3591	114	130	131	23.0	57.1	50.7	50.1
K	340.2	181.0	193.5	3.50	4.13	3.92	5.9	6.1	5.98	5.98
Mg	121.2	53.7	54.9	7.0	6.20	6.06	11.1	11.4	11.1	11.0
Ca	5236	2482	2536	15.4	11.3	11.2	32.1	41.3	40.5	41.2
Fe	0.73	0.2	4.79	0.02	<0.05	0.13	0.01	0.02	<0.05	0.08
Mn	7.75	3.75	3.64	<0.02	<0.03	<0.03	0.01	0.04	0.03	0.04
Al	-	<0.1	<0.1	-	0.09	0.06	-	-	<0.05	0.07
SiO <sub>2</sub>	-	10.4	11.1	-	9.41	9.24	-	-	9.26	9.58
HCO <sub>3</sub>	-	150	-	-	422	-	-	-	344	-
F	-	<0.1	-	-	0.83	-	-	-	0.69	-
Cl	24600	17200	-	-	44.9	-	-	-	14.0	-
Br	316	-	-	-	-	-	-	-	-	-
NO <sub>3</sub>	72	-	-	-	-	-	-	-	-	-
SO <sub>4</sub>	-	106	-	-	21.2	119*	-	-	5.37	7.33*
TDS	38110	18740	-	-	650	-	-	-	482	-
Na/K	21.6	19.2	18.6	32.6	31.5	33.4	3.90	9.36	8.46	8.38
Na/Li	104	83.7	89.8	760	929	936	256	634	461	456
pH	7.32	6.89	-	-	7.74	-	-	-	7.54	-
ionic balance (%)	-6.8	-8.4	-	-	-7.3	-	-	-	-1.8	-
flow (L/min)	5	-	-	-	2	-	-	-	1.5	-
discharge T <sup>o</sup> C	16	-	-	-	6	-	-	-	9	-

All concentrations given as mg/L; - indicates not determined. Cations determined by ICP and AAS; anions (except HCO<sub>3</sub>) by ion chromatography; HCO<sub>3</sub> by titration and SO<sub>4</sub><sup>2-</sup> by ICP (calculated from 2S).

Green Grove Sandstone–Collering Sandstone; Day, 1970) where a minor NW–SE trending fault (downthrow approx 30 m to SW) crosses the River Irthing. This fault is one of a number of similar faults which form the NW part of the Blenkinsopp Boundary Fault system (Trotter and Hollingworth, 1932), occurring close to the intersection of the Stublick and Pennine fault systems. Haydon Spa is situated on the south bank of the River Tyne east of Haydon Bridge, and issues from the approximate horizon of the Namurian Corbridge Limestone (Pendleian; Upper Limestone Group). It lies 500 m due south of a major dyke-filled fault trending 080° which downthrows south approximately 100 m, and which lies 3 km north of the Stublick Fault. Both springs occur within the Northumberland Trough, close to its southern margin.

For all waters, two samples were taken in tightly closed polythene bottles. To one of these approximately 2.5 mL/L of sample of concentrated (10M) AnalaR HNO<sub>3</sub> was added, and both samples were subject to analysis using ICP and AAS techniques (cations). Anions were determined for non-acidified samples, using volumetric and ion chromatographic methods. The results obtained are given in Table 1. The Weardale springwater alone

showed differences between the acidified and non-acidified samples, due to the dissolution of a ferruginous precipitate which was observed to form immediately on sampling. For this water, data for both treated and untreated samples are given in Table 1.

#### Interpretation of the compositional data

On inspection, it is immediately apparent that the Weardale springwater differs from the other samples by having a very much greater total solute content (10<sup>5</sup> mg/L cf. 10<sup>2</sup> mg/L), and that this has decreased by a factor of almost 2 between early 1988 and early 1989, without disturbing the proportions of the major components. Where data are available, all samples have similar contents of silica (approximately 10 mg/L SiO<sub>2</sub>). In contrast to the Weardale sample, the low salinity Gilsland Spa and Haydon Spa samples represent relatively shallow groundwaters.

The compositional data for the three spring water samples have been used with several available chemical geothermometers (Truesdell, 1984) to provide an estimate of the temperatures at which they equilibrated with their wall rocks (Table 2). The geothermometers which involve

the use of Na and K contents assume that the fluids preserve the effects of equilibrium with mineral assemblages which include alkali feldspars, and, with the addition of Ca, calcic feldspar and calc-silicate alteration products. Strictly speaking, it is not appropriate to use these geothermometers with the Gilsland and Haydon Spa samples, in view of the origin of these waters from sequences which consist of mature sediments in which clays and carbonates dominate, with relatively minor feldspar. The geothermometers are not intended for waters of this type. However, the values obtained for the Weardale springwater are reasonable, in view of the geological setting and the proximity of the Weardale granite, and the close agreement for samples taken a year apart indicates that the fluid circulation system is relatively stable, although with variable dilution. An equilibration temperature of approximately

solubilities at 150°C are of the order of 130 mg/L and 180 mg/L SiO<sub>2</sub> respectively (Truesdell, 1984). All of the water samples considered here are saturated with respect to quartz and to a lesser extent chalcedony, under surface or near-surface conditions.

### Comparison with other waters

Elsewhere in granitic areas within the British Isles saline, thermal, waters have been reported from the Carnmenellis granite and its aureole, in particular from South Crofty mine (Alderton and Sheppard, 1977; Edmunds *et al.*, 1984). In terms of total solute content, the Weardale sample approaches values reported for waters from South Crofty and Wheal Jane mines, and greatly exceeds those reported for Mount Wellington and Pendarves mines. It is also relatively rich in Li, with a Li:Cl ratio of approximately 1:300. In order to compare data for samples of granite associated waters from SW England with that from Weardale, a plot of Na/Li against Na/K is given in Fig. 1. The use of this plot overcomes the need to consider dilution and differences in total solute content; it also permits comparison with data for fluid inclusions, which are normally expressed as ratios (e.g. Rankin and Graham, 1988). In Fig. 1 it can be seen that granite-associated waters from Mount Wellington, South Crofty and Wheal Jane mines and Weardale form a population which is characterised by a high Li content relative to Na. In contrast, waters from Pendarves mine form a separate population, with relatively low Li contents, a characteristic noted by Edmunds *et al.* (1984) and which may reflect a short residence time within granite. When data for the north Pennine fluorite fluid inclusions (Rankin and Graham, 1988) are included they can be seen to coincide with and extend the population initially defined by the Pendarves waters. In order to explore further this difference in characteristics between the Weardale springwater and North Pennine fluorites, data for waters from Gilsland and Haydon Spa are combined with those waters from the Coal Measures of NE England (Edmunds, 1975) and for thermal waters from the Derbyshire Dome (Edmunds, 1971) and are shown in Fig. 2. Bearing in mind that sea water has an Na/Li ratio of approximately 60000 it can be seen that the majority of these data form a single overall population with Na/Li varying from 100 to 3000 and Na/K varying from 1 to 100. In some cases, deviation towards higher Na/Li can be explained by possible contamination by sea water or related brines—Na/Li is a sensitive parameter. However, it is remarkable that these data

Table 2. Calculated alkali equilibrium temperatures (°C) for North Pennine spring waters

	Gilsland	Haydon	Cambokeels 1988 1989		equilibria between:
T-NaK(F)	132	233	159	169	feldspar, mica
T-NaK(T)	86	207	117	129	feldspar, mica
T-NaKCa	124	162	158	159	Na-K-Ca feldspar epidote, calcite
T:Q	37	38	-	43	quartz
T-Chalc	3.9	5.1	-	7.8	chalcedony

150°C is considered reasonable in view of the agreement between the three geothermometers. This suggests that a component of the water issuing from the Weardale spring originated from depths of approximately 4 km (assuming a regional geothermal gradient of 35°/km: Dunham, 1987), and may have risen to the surface via the Slitt Vein fracture system. The discharge temperature (16°C) exceeds ambient surface temperatures, supporting the possibility of deep circulation and incomplete thermal equilibration prior to discharge.

The silica geothermometers are based on experimentally determined solubilities (e.g. Rimstidt and Barnes, 1980), and for all samples yield a temperature of approximately 40°C for quartz and 3–8°C for chalcedony; quartz and chalcedony

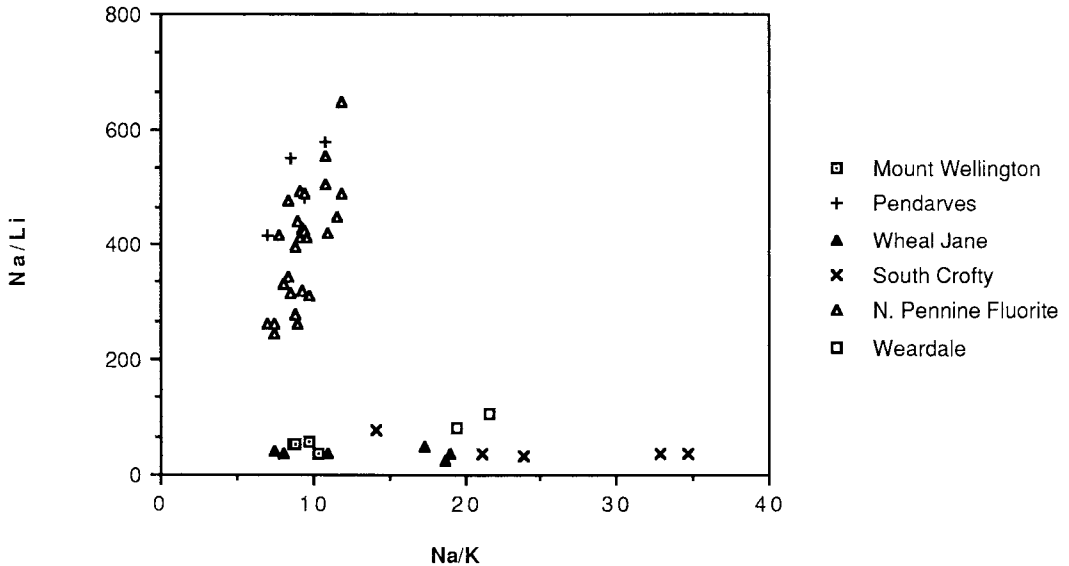


FIG. 1. Compositions of granite-associated minewaters and the Weardale springwater (this paper; Edmunds *et al.*, 1984) and fluid inclusions from North Pennine fluorites (Rankin and Graham, 1988) plotted as Na/K against Na/Li.

show such a consistent overall trend, which may reflect one appropriate for groundwaters hosted by shale and limestone-dominated lithologies. These compositions can be regarded as lying on trends defined by mixing of extreme compositions, and because of the use of ratios these trends are not linear, but curve depending on the Na/Li and Na/K ratios of the mixture end members. Dilution does not displace plots in this type of graph.

Although Li, Na and K demonstrate similarities between the Weardale springwater and granite-associated springwaters from southwest England, Br and Cl suggest that the Weardale water also has affinities with saline-minewaters derived from the Coal Measures of northeast England (Edmunds, 1975). Fig. 3 shows a plot of log Cl against log Br for granite-associated waters from southwest England and for waters derived from northeast England Coal Measures. Compared to a value for sea water, the Coal Measures waters have higher Cl and Br contents, while those for the southwest England granite-associated waters are lower. The Weardale spring water plots with the Coal Measures waters rather than the southwest England granite-associated waters. In addition to being more saline, the Weardale spring water is enriched in Br relative to Cl. By analogy with Edmunds' (1975) interpretation of Br levels in Coal Measure brines it is considered that the relative enrichment in Br shown by the

Weardale springwater arises as a consequence of interactions with organic matter. This is consistent with reported high levels of methane within Cambokeels mine, which is believed to be derived from the spring water (Dunham, in press).

#### Metallogenetic significance of the Weardale springwater

By comparison with granite associated thermal waters from SW England, it is apparent from the data for Na, K and Li that a component of the Weardale springwater is probably derived from within the Weardale Granite, which lies approximately 80 m below the site of sampling. \*The Weardale granite is known to be a 'high heat production granite', and shares many geochemical and mineralogical characteristics with those of SW England (Brown *et al.*, 1987; Webb *et al.*, 1985). In particular, the high Li content of the Weardale granite, due to the presence of a Li rich mica, is distinctive and is responsible for the relatively high Li content of the mine water (cf. Edmunds *et al.*, 1984, who conclude that Li-rich biotite accounts for the origin of the elevated Li contents of waters from South Crofty, Wheal Jane and Mount Wellington mines). In contrast, the Br and Cl data and occur-

\*In addition, a connection with the granite is demonstrated by an association with the spring water of high radon levels.

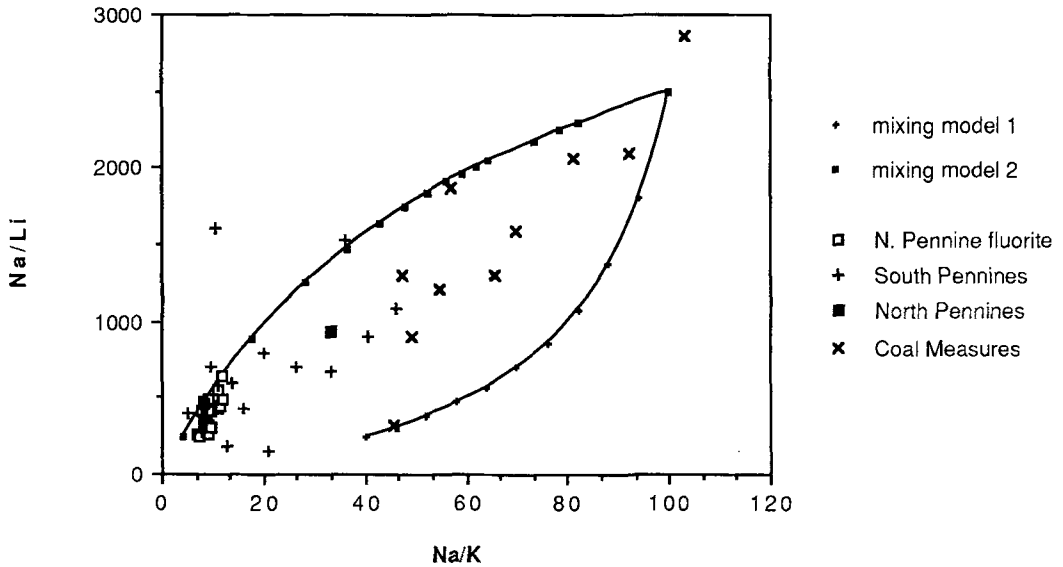


Fig. 2. Compositions of waters derived from Carboniferous sedimentary sequences and fluid inclusions from North Pennine fluorites (Rankin and Graham, 1988) plotted as Na/K against Na/Li. Sources of water compositions: South Pennines—Edmunds, 1971; North Pennines—this paper; Coal Measures—Edmunds, 1975 (excluding samples with Na/Li > 5000). Mixing model 1 shows compositions achieved by mixing two waters with alkali values typical for a Coal Measures source (CM1: Na = 20000 mg/L, K = 500 mg/L, Li = 80 mg/L and CM2: Na = 50000 mg/L, K = 500 mg/L, Li = 20 mg/L), with extrapolation between points at 10% intervals. Model 2 is for mixing compositions analogous to Haydon Spa (H: Na = 25 mg/L, K = 6 mg/L, Li = 0.1 mg/L) with those of the Coal Measures (CM2), using intervals of 0.2% (100% H—98% H) and 1% (98% H—90% H).

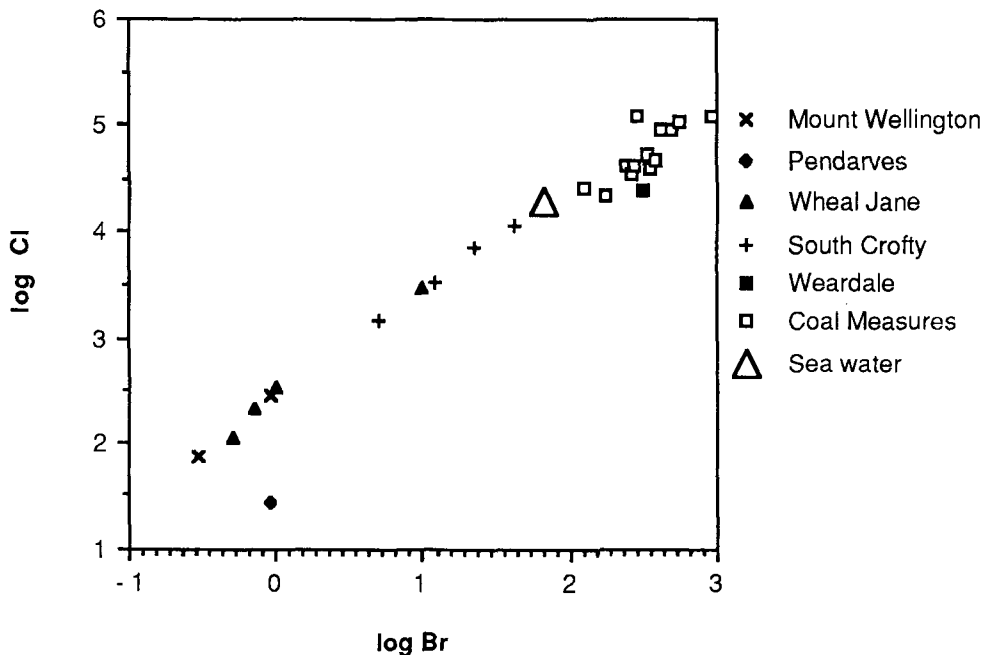


Fig. 3. Plot of log Cl against log Br for granite-associated waters from southwest England and Weardale and for waters from northeast England Coal Measures. Sources of data as in Figs. 1 and 2.

rence of methane suggest that a component of the brine was derived from an organic-rich sequence, similar to the Coal Measures. Suitable lithologies occur locally, as part of the Carboniferous sequence which overlies the Weardale granite, but the possibility that the Weardale brine might ultimately have been derived from Coal Measures sequences adjacent to the Alston Block cannot be ruled out (cf. Edmunds, 1975).

It can be considered that the Weardale springwater represents a composite fluid which attests to at least three stages of evolution. One is dilution by meteoric water, accounting for the variable salinity at different times of sampling. The second reflects interaction with organic-rich sediments and the third reflects reaction with the Weardale granite which appears to have taken place at temperatures of the order of 150°C. The characteristics of the Weardale springwater may be a consequence of one of two processes which cannot be distinguished at this stage. The first possibility involves derivation of water from Carboniferous sequences adjacent to the Pennines followed by circulation through the Weardale granite prior to dilution, and involves large scale circulation. The second involves interaction with overlying Carboniferous sequences, close to the site of the spring, with more limited circulation through the granite.

Composite fluid circulation systems of the type inferred for the Weardale springwater have been proposed for orefluid circulation within the North Pennine orefield. It might be expected that the mineralizing fluids would resemble chemically the present day spring if they had experienced a similar history, especially in view of the similarity between fluid inclusion temperatures (120 to 190°C; Sawkins, 1966) and those derived for the Weardale spring from alkali geothermometers. In particular, in view of possible interaction with the Weardale granite, they would be expected to be rich in Li, because of the low stability of Li-rich micas during granite alteration (e.g. Manning and Exley, 1984), and because of the observed depletions in Li within secondary minerals relative to primary rock-forming minerals (Edmunds *et al.*, 1986). They would also be expected to be enriched in Br relative to Cl if they contained a component derived from organic-rich sediments such as the Coal Measures. However, compositional data for fluorite-hosted fluid inclusions from the North Pennine Orefield are limited to those for Li given by Rankin and Graham (1988), which have been plotted in both Figs. 1 and 2. The inclusion fluids show no clear affinity with the granite-associated waters (Fig. 1), but instead resemble those associated with the Carboniferous sedimentary basins

which flank the North Pennine Orefield, particularly to the east. This observation supports hypotheses which derive the mineralizing fluids from these basins, but suggests that only limited interaction took place within the Weardale granite. As Rankin and Graham (1988) point out, the inclusion fluids are relatively rich in Li compared with the basinal brines, and in Fig. 2 they plot at the Li-rich end of the overall population. In order to reconcile these observations it is considered possible that the fluids responsible for fluorite mineralization may indeed have passed through the Weardale granite, or incorporated a component derived from that aquifer, but that the Weardale springwater reported here represents a fluid which has undergone considerably more interaction with the granite. It may either have had a longer residence time within the granite aquifer, or contain a higher proportion of granite-derived water. Consequently, at the time of mineralization, the influence of the granite may have been mainly as a source of heat rather than chemical constituents, focusing the ascent of mineralizing fluids derived from adjacent sedimentary sequences. The mineralizing fluids may have risen too rapidly to achieve the degree of chemical equilibrium observed for the present day spring, despite faster equilibration at high temperatures. Data for Br from north Pennine fluid inclusions are clearly necessary to provide further evidence of the origin of the mineralising fluids.

The apparent inconsistency between the alkali geothermometers and the silica geothermometers suggests that the Weardale springwaters have preserved to some extent alkali ratios appropriate for reactions involving feldspars and micas at depths of the order of 4–5 km, for which dissolved silica contents are expected to be of the order of 130–180 mg/L. The low silica contents of the spring waters (approximately 10 mg/L) on the other hand indicate that quartz or chalcedony has precipitated between those depths and the site of the spring. It is possible that a proportion of the silica found as a cement within brecciated fluorite from the North Pennine orefield could have precipitated from spring waters of this type, and that quartz and chalcedony cementation of the fluorite mineralization could be a continuing process. Using the solution modelling package EQ3 (Wolery, 1983) for temperatures of 25°C and 150°C, it is also apparent that the Weardale spring water is undersaturated with respect to both fluorite and gypsum and is saturated only with respect to quartz (and the other silica minerals) at 25°C. Apart from the data for silica, these observations reflect the dilution of the springwater by meteoric water. However, the comparatively high dis-

solved silica contents may arise as a consequence of the derivation of the spring from a mineral vein in which both quartz and chalcedony occur.

### Conclusions

It has been demonstrated that, in terms of alkalis, the Weardale springwater closely resembles saline mine waters reported from granitic areas within southwest England, while data for Br and Cl suggest an affinity with saline waters derived from Carboniferous sequences within and adjacent to the Pennines. By analogy with other waters, many of the chemical characteristics of the Weardale springwater are believed to have arisen as a consequence of fluid-rock reactions both within the Weardale granite and within adjacent organic-rich sediments. These observations imply that it should be possible to recognize characteristics which indicate interaction between ancient fluids and granite or sediment within compositional data for fluid inclusions from North Pennine fluorites, which would be expected to resemble the Weardale springwater in composition if they had a similar hydrological history. However, consideration of available data for Na, K and Li suggests that the ore-forming fluids predominantly resemble waters derived from Carboniferous sequences, with only a minor component from the granite; Br and Cl data for inclusion fluids are required to explore this possibility further. The ore-forming fluids may have circulated through the Weardale granite relatively rapidly, or contain a much less significant component of granite-derived water than the present day spring water. It is also clear that although the Weardale springwater preserves alkali ratios appropriate for equilibrium with granite at 150°C it is undersaturated with respect to silica at that temperature. Consequently, quartz or chalcedony seem to have precipitated between source and surface, raising the possibility that silica cementation of fluorite may be a continuing process within the orefield.

### Acknowledgements

We would like to thank W. M. Edmunds for his valuable comments on the manuscript and D. A. Polya for his assistance with EQ3.

### References

- Alderton, D. H. M. and Sheppard S. M. F. (1977) Chemistry and origin of thermal waters from southwest England. *Trans. Inst. Min. Metall. (Sect B Appl. Earth Sci.)*, **86**, B191-4.
- Brown, G. C., Ixer, R. A., Plant, J. A., and Webb, P. C. (1987) Geochemistry of granites beneath the north Pennines and their role in orefield mineralization. *Ibid.* **96**, B65-76.
- Day, J. B. W. (1970) *The geology of the country around Bewcastle*. Mem. Geol. Surv. **12**, 357 pp.
- Dunham, K. C. (1949) *Geology of the Northern Pennine Orefield*. Vol 1, Tyne to Stainmore. Economic Mem. Geol. Surv., 357 pp.
- (1983) Ore genesis in the English Pennines: a fluorite subtype. In *International conference on Mississippi Valley type lead-zinc deposits, proceedings volume* (Kisvarsanyi G. et al. eds). Rolla, Missouri: University of Missouri Press, 86-112.
- (1987) Discussion of Brown et al., *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)*, **96**, B229-30.
- (in press) *Geology of the Northern Pennine Orefield*. Vol. 1, Tyne to Stainmore (second edition). Economic Mem. British Geol. Surv.
- and Wilson A. A. (1985) *Geology of the Northern Pennine Orefield*. Vol. 2, Stainmore to Craven. Economic Mem. British Geol. Surv., 247 pp.
- Edmunds, W. M. (1971) *Hydrogeochemistry of groundwaters in the Derbyshire Dome with special reference to trace constituents*. Rep. no. 71-7, Inst. Geol. Sci., 52 pp.
- (1975) Geochemistry of brines in the Coal Measures of northeast England. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)*, **84**, B39-52.
- Andrews, J. N., Burgess, W. G., Kay, R. L. F. and Lee, D. J. (1984) The evolution of saline and thermal groundwaters in the Carnmenellis granite. *Mineral. Mag.* **48**, 407-24.
- Cook, J. M. and Miles, D. L. (1986) Lithium mobility and cycling in dilute continental waters. Extended abstracts of Water-Rock Interaction V. Reykjavik, 183-7.
- Manning, D. A. C. and Exley, C. S. (1984) The origins of late-stage rocks in the St Austell granite—a reinterpretation. *J. geol. Soc. London*, **141**, 581-91.
- Rankin, M. J. and Graham, M. J. (1988) Na, K, and Li contents of mineralizing fluids in the Northern Pennine Orefield, England, and their genetic significance. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)*, **97**, B99-107.
- Rimstidt, J. D. and Barnes, H. L. (1980) The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta*, **44**, 1683-99.
- Sawkins, F. J. (1966) Ore genesis in the North Pennine orefield, in the light of fluid inclusion studies. *Econ. Geol.* **61**, 385-401.
- Trotter, F. M. and Hollingworth, S. E. (1932) *The geology of the Brampton district*. Mem. Geol. Surv. **18**, 223 pp.
- Truesdell, A.H. (1984) Chemical geothermometers for geothermal exploration. In *Fluid-mineral equilibria in hydrothermal systems* (Henley, R. W., Truesdell, A. H. and Barton, P. B. Jr. eds.) *Reviews in Econ. Geol.* **1**, 31-44.
- Webb, P. C., Tindle, A. G., Barritt, S. D., Brown, G. C., and Miller, J. F. (1985) Radiothermal granites of the United Kingdom: comparison of fractionation patterns and variation of heat production for selected granites. In *High heat production (HHP) granites*,

*hydrothermal circulation and ore genesis*, Inst. Min. Metall., 409–24.

Wolery, T. J. (1983) *EQ3NR, a computer programme for geochemical aqueous speciation–solubility calculations: user's guide and documentation*. UCRL-53414,

Lawrence Livermore Laboratory, Livermore, California.

[Manuscript received 16 October 1989;  
revised 9 February 1990]