Natural Environment Research Council

Institute of Geological Sciences

Mineral Reconnaissance Programme Report

No. 7
**Investigation of tungsten
and other mineralisation
.associated with the
Skiddaw Granite near
Carrock Mine, Cumbria**

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Investigation of tungsten and other mineralisation associated with the Skiddaw Granite near Carrock Mine, Cumbria

J. D. Appleton, BSc, PhD and A. J. Wadge, MA

London: 1976

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incorporation of the Geological Survey of Great Britain
and the Museum of Practical Geology with
Overseas Geological Surveys and is a constituent body
of the Natural Environment Research Council.

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Summary

The tungsten mineralization at Carrock Mine is closely associated with a greisenized cupola of the Skiddaw Granite and initial investigations were directed to testing other cupolas in its upper surface for tungsten veins. The analysis of stream sediments, panned concentrates and rock samples indicates anomalous tungsten and arsenic values from an area west of the mine. Attention to this particular area has also been drawn by recently published fluid inclusion and isotope work which suggests that the mineralisation was caused by the circulation of large volumes of brine through fissured rocks along the northern margin of the granite. Further exploration is suggested which would test the potentiality of the anomalous area.

Investigation of tungsten and other mineralisation associated with the Skiddaw Granite near Carrock Mine, Cumbria

J. D. Appleton and A. J. Wadge

INTRODUCTION

Carrock Mine is situated in the northern Lake District about 20 km west of Penrith and 10 km north-east of Keswick, in open fell-country generally about 450 m (1500 ft) above O.D. and rising to 932 m (3058 ft) on Skiddaw and to 870 m (2853 ft) on Saddleback (Fig.1a). The mine lies in the narrow valley of Grainsgill Beck, a tributary of the River Caldew. A metalled road leads to the mine from the east and a rough track continues farther up the Caldew valley, but otherwise the high relief and rough terrain limit vehicular access to the surrounding fells. The area lies within the Lake District National Park.

GEOLOGY

Detailed accounts of the geology of the district (Eastwood and others 1968) and of the Skiddaw granite (Hitchen 1934) are summarized below.

Underlying most of the area are rocks of the Skiddaw Group consisting of turbiditic greywackes, dominantly of mudstones and silt grade but also including bands of greywacke-sandstone. The full thickness of the sequence has not been proved, but at least several **hundred** metres are present. Rare graptolite faunas show that the succession is of Lower Ordovician (Arenig-Llanvirn) age. Outcrops are mainly affected by upright, open folding, trending east-north-east and probably due to end-Silurian earth movements, but complex minor structures produced by polyphase folding are also present (Roberts 1971).

A thick volcanic succession of massive andesites with tuffs and agglomerates, totalling more than 2000 m, is present in the north of the area. These beds have generally been taken to correlate with the Borrowdale Volcanic Group of the southern Lake District and the name has been retained here, although microfaunal evidence suggests that the sequence may be similar in age to some of the younger Skiddaw sediments of other areas (Downie & Soper 1972). The beds strike generally east-west and at outcrop dip steeply to the north; recent magnetic work suggests however that at shallow depths the regional dip of this sequence is steeply to the south. In any event, there is no doubt that the volcanics form a near-vertical zone of massive, well-jointed rocks along the northern margin of the outcrop of the Skiddaw Group sediments. The volcanics are unconformably overlain by the upper Ordovician (Caradocian) Drygill Shales.

Two major intrusions cut the country rocks. The Carrock Fell complex of gabbro, granophyre and diabase trends roughly east-west along the regional strike and has steeply dipping margins. Its age is upper Ordovician or Silurian and it
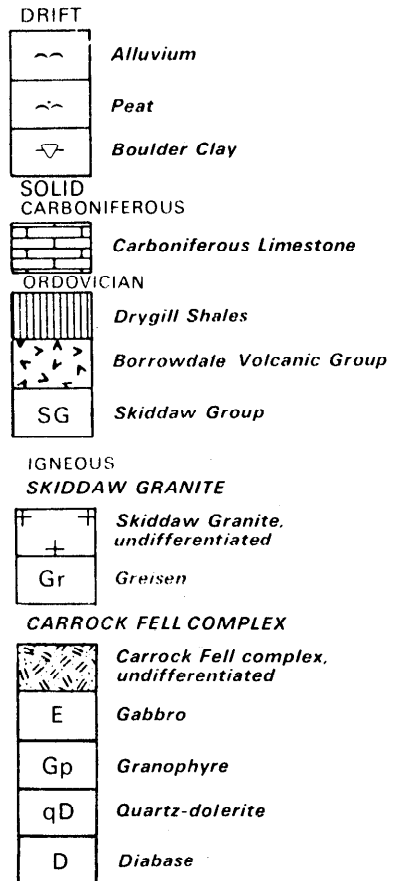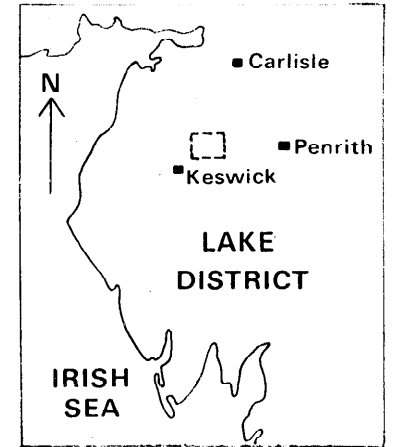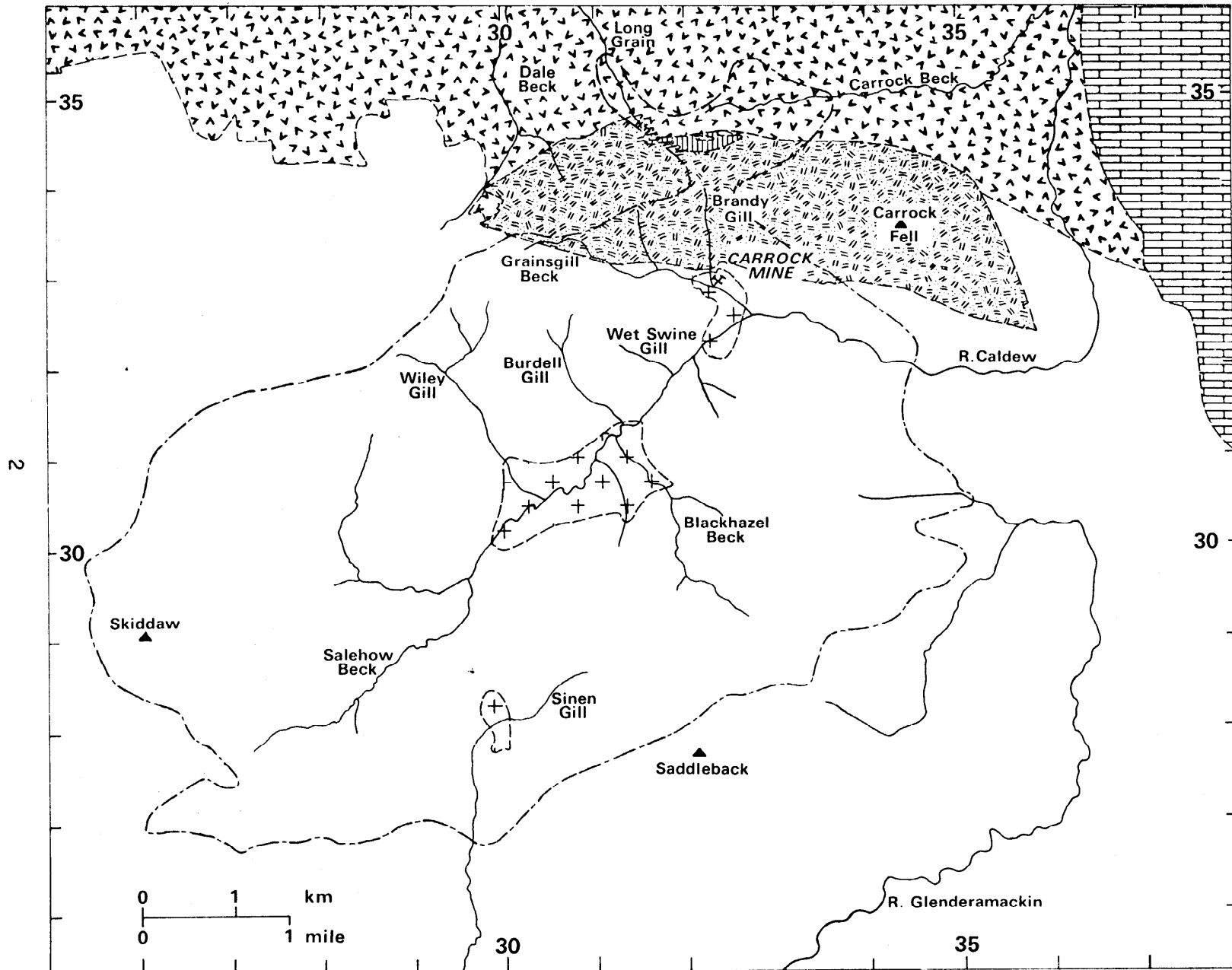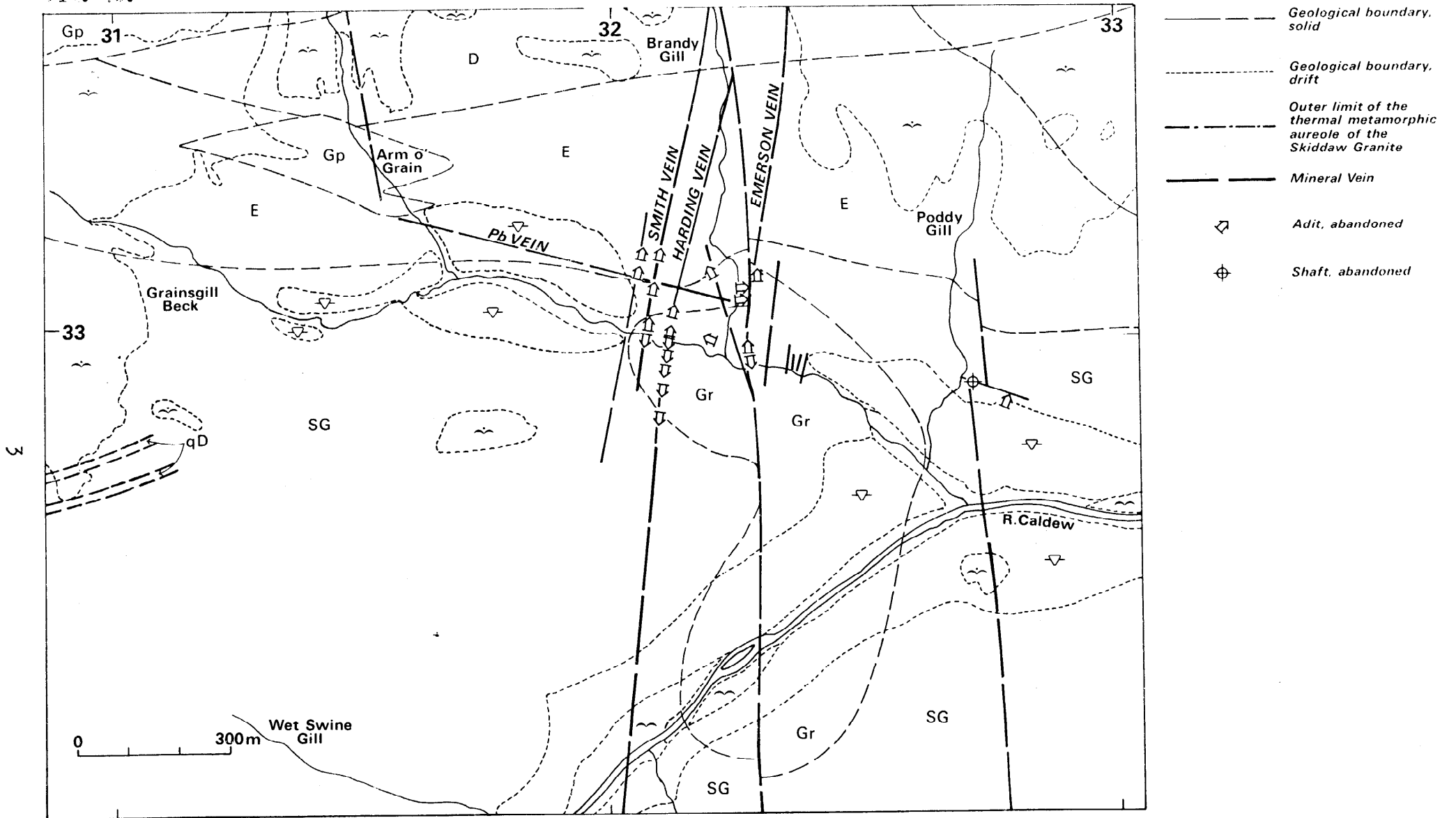
Fig. 12.

Fig. 1h.

Fig. 1 (a) General geology of the Carrock Fell district

(b) Detailed geological map of the area around Carrock Mine

pre-dates the other major intrusion, the end-Silurian Skiddaw Granite. The latter is only partly unroofed but its metamorphic aureole forms a flat-topped dome with steep sides and probably corresponds generally to the form of the upper surface of the granite.

FORMER MINING

Mining began in the area in 1854 (Shaw 1975) with small workings on an E-trending lead vein just north of Grainsgill Beck. In the first decades of the present century three N-trending tungsten veins were exploited (Fig 1b). Profitable working throughout the 1914-18 War ended with a slump in tungsten prices in 1919. During this time five south-bank levels and No. 1 North Level were driven on the Harding Vein (Fig. 2) and associated stopes were worked; in addition, two levels and open-cut workings on the Emerson Vein exploited good ore on the north side of the Beck. The mine was re-opened in 1942 by Non-Ferrous Minerals Development Ltd. on behalf of the Ministry of Supply, and a new adit and No. 2 North Level were driven on the Harding Vein. Quoted assay values (Fig. 2) were determined at this time. By 1944 overseas supplies of tungsten were assured and the mine was closed. In 1972, an increase in world prices encouraged a Canadian company, World Wide Energy Co. Ltd. of Calgary, to re-open the mine and install a mill. Twenty-two men were employed at the mine from June to August 1972 but suddenly all work was abandoned. It is understood that the parent company's financial difficulties were unconnected with the Carrock venture, and pre-production trials at the mine were proceeding satisfactorily just prior to closure. The mine is currently kept on a care and maintenance basis.

PRESENT INVESTIGATIONS

The proposal to investigate the Carrock tungsten occurence was initiated in 1973 and was based upon the following model. It was recognized that the known tungsten-bearing veins were closely associated with a greisenized cupola of the Skiddaw Granite, cropping out in Grainsgill Beck, and it seemed clear that they were derived from hydrothermal fluids that had been concentrated in the uppermost parts of the granite, locally altering it to greisen. It was supposed that the fluids were expelled upwards from the granite magma at a late stage in its cooling. If the height of the top surface of the granite was indeed a major controlling factor in localising the fluids, then other cupolas might well be greisenized and mineralised, particularly as there was nothing to suggest that the Grainsgill cupola was significantly higher than other cupolas in the Caldew valley and Sinen Gill. The main objective of the work was thus to test the other granite outcrops in the area for tungsten-bearing veins. At an early stage a limited amount of greisen was noted in the field at several exposures, particularly in the upper Caldew valley where the largest cupola is mainly covered by drift.

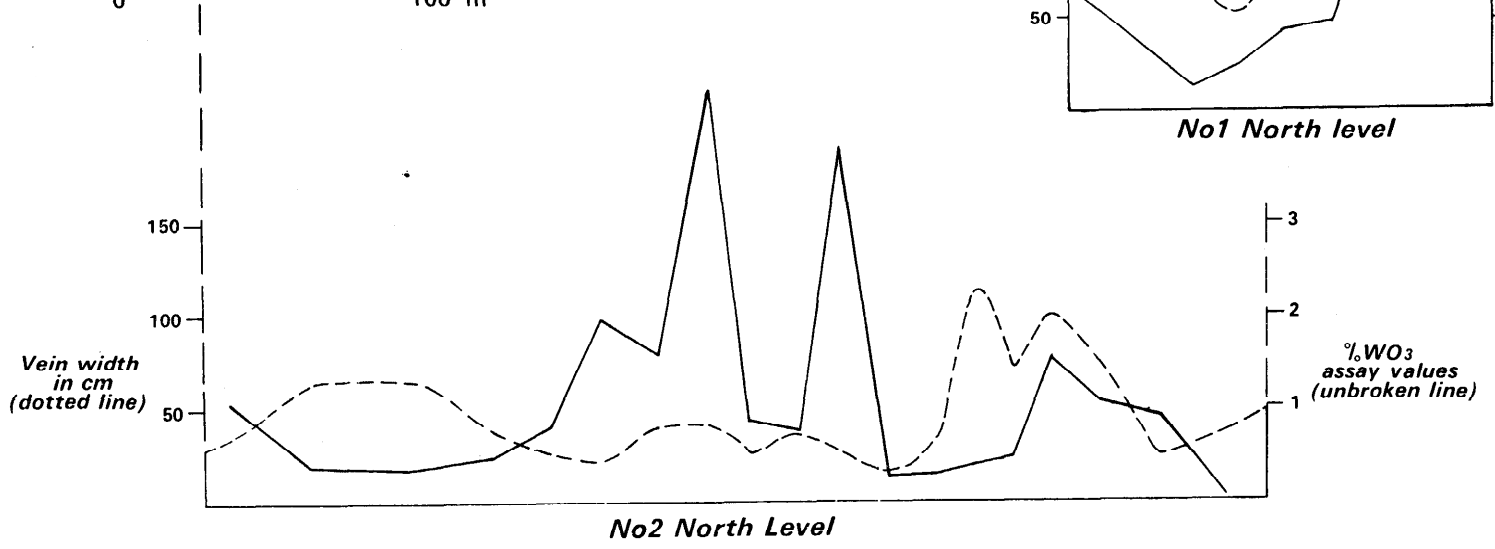As an additional objective it was proposed to test the greisen outcrops in
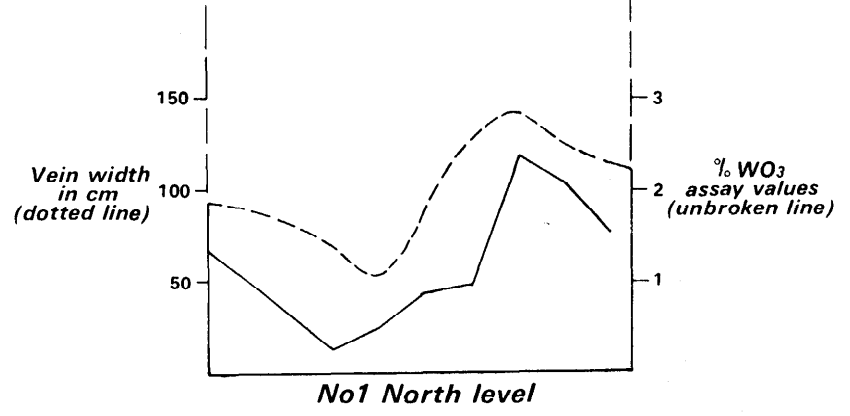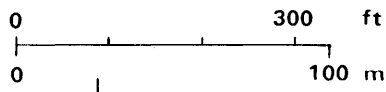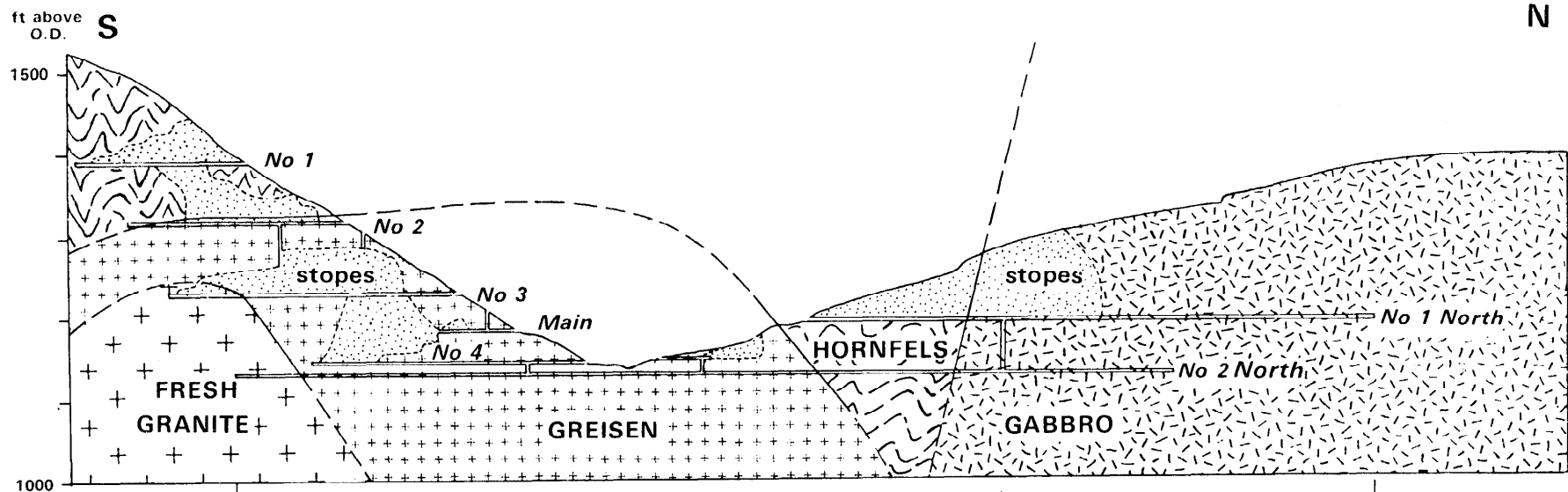
Fig. 2. Horizontal section along the Harding Vein showing vein widths and tungsten values

Grainsgill Beck and elsewhere to see if the altered granite contained sufficient disseminated tungsten to constitute a large-volume, low-grade ore.

The principal method of investigation was the geochemical sampling described below, but supporting work was also undertaken to clarify the conditions in which mineralisation had taken place. This work on the fluid inclusions, oxygen isotopes and K/Ar age has been described elsewhere (Shepherd and others 1976), a copy of which is appended to this report. In addition, the field investigations included checking the published 6-inch geological maps of the area and examining the accessible workings at Carrock Mine. Mine-plans, sections and assay values from the Institute's archives have all been used in compiling this report.

Sample collection, preparation and analysis

Geochemical investigations were based on stream sediment and panned concentrate samples collected at 84 sites by Dr I R Wilson assisted by Mr M McGlashan and a party of voluntary workers. Rock samples were collected by Dr J D Appleton and Dr T J Shepherd. Sample collection and preparation methods have been described by Plant (1971), Plant and Rhind (1974) and Leake and Aucott (1973). Stream sediments and rock samples were analysed for W by a colorimetric method, for Cu, Pb and Zn by atomic absorption spectrometry (AAS), and for U by induced neutron activation (INAA). A selection of the sediments was analysed for thirty five elements including W, Mo, Au and As by INAA. The panned concentrates were analysed for Ce, Ba, Sb, Sn, Pb, Zn, Cu, Ni, Fe, Mn and Ti by X-ray fluorescence spectrometry. Zn, Cu and Pb in water were determined by AAS and for U in water by INAA.

Statistical Analysis

Twenty stream sediment samples were analysed for thirty five elements by INAA but only Zn, As, Ba, W, Ti and Mn showed significant variation. Summary statistics are given in Table 1.

Table 1

Summary statistics for twenty stream-sediment samples analysed by the induced neutron activation method (INAA)

Element	Range		Arithmetic		Log_{10} Units		Geometric		
	Min	Max	$\overline{X}$	σ	$\overline{X}$	σ	$\overline{X}$	$\overline{X}+1$	$\overline{X}+2$
Zn	100	1110	380	261	2.489	0.291	308	603	1178
As	5	1094	294	310	2.205	0.561	160	582	2123
Ba	511	1130	821	150	2.907	0.083	807	977	1183
W	1	396	38	89	1.033	0.668	11	53	234
Ti	2000	19240	5441	3869	3.653	0.273	4498	8433	15812
Mn	1455	16930	6580	4174	3.728	0.298	5345	10616	21086

Based on log-transformed data, the following correlations are significant: Zn-Ba (99% level), Zn-W (95% level) As-W (99.9% level).

After the INAA tungsten results became available, a further eighteen sediments were analysed for W by a colorimetric method together with seven samples that had already been analysed by INAA. There was good correspondence between the results of the two analytical methods. Arithmetic data distributions are positively skewed so a log-transform was applied before correlation coefficients were calculated. Fig. 3 shows the position of thirty three stream sediment samples analysed for W (three samples omitted from Wet Swine Gill for clarity).

Table 2
Summary statistics for samples analysed for tungsten
(n = 36*)

Element	Range		Arithmetic		Log_{10} Units		Geometric		
	Min	Max	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	$\bar{X}+1$	$\bar{X}+2$
Stream Sediments									
W	0	5700	258	945	1.514	0.895	33	256	2013
Cu	30	230	63	39	1.741	0.208	55	89	143
Pb	40	1750	264	387	2.217	0.366	165	383	889
Zn	40	900	384	219	2.501	0.300	317	632	1261
Panned Concentrate									
Ba	25	21082	2110	3648	2.956	0.617	904	3741	15488
Sn	0	24	7	6	0.739	0.387	5	13	33
Pb	45	12142	933	2010	2.638	0.497	434	1365	4285
Zn	53	1975	499	385	2.569	0.365	371	859	1990
Cu	9	588	153	149	1.979	0.454	95	271	770
Fe	2.986	21.19	10.93	4.41	0.998	0.203	9.95	15.88	25.35
Mn	0.044	3.82	1.02	0.82	0.145	0.415	1.39	3.63	34.28

* Two of the 38 analyses were not included because of sample contamination

Table 3

Correlation coefficients for samples analysed for tungsten

(n = 36*)

Element	Correlation coefficient significant at:		
	95-99% level	99-99.5% level	> 99.5% level
W	Pb	Sn	Cu, Zn, Cu, Fe, Mn
Cu	Fe	Zn, Ba	W, Sn, Pb, Zn, Cu
Pb			Zn, Pb
Zn	Zn	Cu	Pb
Ba		Cu	Pb, Zn, Cu, Mn
Sn	Pb, Zn, Cu	W	Cu
Pb	Pb, Sn		Cu, Pb, Ba, Zn, Cu, Fe, Mn
Zn	Zn, Sn		W, Cu, Ba, Pb, Cu, Fe, Mn
Cu	Sn		W, Cu, Ba, Pb, Zn, Fe, Mn
Fe	Cu		W, Pb, Zn, Cu, Mn
Mn			W, Ba, Pb, Zn, Cu, Fe

Note   Data for panned concentrate samples are underlined.
        Correlation coefficients based on log-transformed data.

* Two of the 38 analyses were not included because of sample
  contamination.

Table 4

Summary statistics for all samples

(n = 84)

Element	Range		Arithmetic		Log_{10} Units		Geometric		
	Min	Max	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	$\bar{X} + 1$	$\bar{X} + 2$
Cu	20	230	54	30	1.694	0.180	49	75	113
Pb	30	2150	241	346	2.208	0.339	161	352	769
Zn	40	900	326	186	2.437	0.272	273	512	959
Ba	25	21416	2635	4104	3.037	0.602	1089	4355	17418
Sn	0	61	7	8	0.659	0.409	5	12	30
Pb	42	12156	1036	2102	2.648	0.535	445	1524	5224
Zn	53	1975	449	375	2.514	0.361	327	750	1722
Cu	9	884	160	180	1.943	0.494	88	274	853
Fe	3.00	21.20	10.11	4.43	0.959	0.210	9.10	14.76	23.93
Mn	0.0	3.90	1.03	0.93	1.169	0.439	0.15	0.40	1.11
U	1.9	10.8	3.15	1.66	0.482	0.173	3.04	4.52	6.74
U)in	0	0.03	-	-	-	-	-	-	-
Zn)water	0	6.15	-	-	-	-	-	-	-

The class intervals used for plotting selected elements in stream sediments and panned concentrates are based on geometric mean plus one and two standard deviations (Figs. 3-12, 14). Exceptions are U in sediment (Fig. 15) and Zn in water (Fig. 13) where there are too many values below the detection limit for geometric means and standard deviations to be calculated.

Tungsten

In addition to high tungsten values below Carrock Mine, moderately high values were recorded in Wet Swine Gill and Burdell Gill (Fig. 3). A grab-sample from a N-S trending manganese-quartz vein from the head of Burdell Gill contains 1200 ppm W and a grab-sample from a quartz-manganese-arsenopyrite vein from the head of Wet Swine Gill assayed 6600 ppm W. Tungsten phases were not identified in either vein but wolframite and scheelite are present in panned concentrates from both streams. The veins are probably low temperature extensions of the Carrock-type tungsten veins.

Five samples of greisenised granite from Grainsgill Beck and the River Caldew contained 2-10 ppm W while a specimen of greisen from Carrock Mine assayed 15 ppm W (See Appendix I Fig. 2, Table 6).

Arsenic

Highly anomalous arsenic values up to 1100 ppm were detected in stream sediments from Wet Swine Gill, Burdell Gill and Wiley Gill (Fig. 4); the correlation between tungsten and arsenic was found to be significant at the 99.95% level. The occurrence of anomalous arsenic in Wiley Gill, 1 km west of anomalous tungsten values, suggests that there is an arsenic halo around the tungsten mineralisation. This arsenic halo is observed on a smaller scale in greisen adjacent to the Carrock Mine tungsten veins (See Appendix I).

Gold

Traces of gold were detected in two stream sediment samples (Fig. 4); the higher value of 0.15 ppm was from the River Caldew above the confluence with Wet Swine Gill, while the lower value of 0.06 ppm was detected 0.5 km west of Carrock Mine. The only previously recorded gold occurrence in the Lake District is the Goldscope copper mine where gold is reputed to be associated with silver (Eastwood and others 1968).

Molybdenum

Although molybdenite occurs in the Carrock Mine tungsten veins (Hitchen, 1934), molybdenum in stream sediments is below the detection limit of 5 ppm except in the lower reaches of Blackhazel Beck where a value of 10 ppm was recorded.

Tin

Tin in pan concentrates was generally below the detection limit of 7 ppm though slightly anomalous values up to 61 ppm were detected below Carrock Mine and in Grainsgill Beck (Fig. 5). The correlation with tungsten is not significant at the 95% level.

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Barium, copper, lead, zinc, iron and manganese

There is a highly significant (99.5%) correlation between these elements in panned concentrates, the most highly anomalous samples being found in the upper sections of Wiley Gill, Burdell Gill, Wet Swine Gill, Grainsgill Beck and also in the eastern tributary of Blackhazel Beck (Figs. 6-14). It is clear that these anomalies reflect known vein mineralisation (Eastwood et al., 1968) so they were not followed up in detail. Zn, Cu and Pb in water samples do not correlate significantly with the same elements in stream sediments and panned concentrates.

Uranium

Uranium in sediments (Fig. 15) reflects the outcrop of the Skiddaw Granite but uranium in water shows only background variation below a maximum of 3 ppb.

ORE GENESIS

The supporting work (described in Appendix I) has indicated that the tungsten mineralisation was associated with the metasomatic alteration of the Skiddaw Granite soon after its emplacement, but has significantly refined the initial model of mineral genesis. It is now suggested that the tungsten veins and the greisen resulted from the circulation of large volumes of moderately saline NaCl brines through the hot intrusion, and not simply from hydrothermal fluids expelled from the cooling granite, as had been supposed. Analysis of the oxygen isotopes in the vein quartz shows that the brines consisted mainly of formation waters and ground water derived from the country rocks. Some magmatic water was probably also present, since it is difficult to envisage another source for the tungsten, but the proportion is likely to have been small.

Brine circulation seems to have been especially active on the northern margin of the granite where joints and fractures in the massive rocks of the volcanic sequence and the Carrock Fell complex provided open channelways. In contrast, joints and fractures in the Skiddaw Group sediments forming the rest of the country rock were much tighter hydrologically and minimized the circulation. The new model thus indicates that exploration should be directed towards those areas where fissured rocks lie close to the granite, rather than towards cupolas on its upper surface. The new conditions are best fulfilled in the area west of Carrock Mine and it is encouraging that it is from this area that the high tungsten and arsenic values have been obtained.

On a more detailed level, there is evidence that the known veins are wider where the country rocks are more massive. For example, the Harding Vein in Carrock Mine (Fig. 2) is wider in the gabbro than in the hornfels or greisen. The richness of the veins however, appears unaffected by the nature of the country rock (Fig. 2). Only 25 assays, taken at about 20 m intervals along the North levels, are available but they show no systematic variation with lithology.

CONCLUSIONS

(a) Vein mineralisation of the quartz-wolframite-scheelite-arsenopyrite

association occurs in Skiddaw Group rocks in the headwaters of Wet Swine Gill and has been identified in panned concentrates from Burdell Gill where manganese mineralisation is dominant. These veins have been located during the programme, and are similar to those worked at Carrock Mine. They may become wider and richer in tungsten at depths where they pass into more fissured ground in gabbro or greisenized granite.

(b) The arsenic halo to the tungsten mineralisation extends more than 2 km west of the mine and defines a broad zone within which further tungsten-bearing veins may occur; insufficient samples were collected to allow precise delineation of the halo.

(c) The work on fluid inclusions (described in Appendix I, see Table 1) has demonstrated clear chemical differences between quartz from tungsten-bearing veins and that from other veins. Because quartz is the commonest float, this difference provides a useful test of the potential of outcropping veins.

(d) On the basis of a limited number of samples, it appears that the greisenized granite south of Carrock Mine has too low a tungsten content to be a viable low-grade ore.

RECOMMENDATIONS FOR FURTHER WORK

To date no exploration other than the driving of levels on the three veins cropping out in Grainsgill Beck has been undertaken. In the absence of any exploratory drilling, the veins are unproven beyond and beneath the present workings. As there is no known geological reason for expecting a rapid decrease in vein quality either downwards or laterally, it would be sensible to begin exploration by further testing of these known veins.

In the longer term, the area west of the mine should be explored more thoroughly. Samples should be collected from all quartz outcrops and float for fluid inclusion analysis, and resistivity methods used to detect veins which do not reach the surface. Detailed gravity surveys may be useful to define the positions of the granite and gabbro margins and to determine how steeply below the present topography the most favourable lithologies are situated. Finally targets would have to be proved by the drilling of inclined boreholes.

ACKNOWLEDGEMENTS

REFERENCES

DOWNIE, C. and SOPER, N.J. 1972. Age of the Eycott Volcanic Group and its conformable relationship to the Skiddaw Slates in the English Lake District. Geol. Mag., 109, pp. 259-268.

EASTWOOD, T.   1959.   The Lake District mining field.   In: The Future of Non-
ferrous mining in Great Britain and Ireland, 149-174.   Institution of
Mining and Metallurgy, London.

EASTWOOD, T., HOLLINGWORTH, S.E., ROSE, W.C.C. and TROTTER, F.M. 1969.
Geology of the country around Cockermouth and Caldbeck.   Mem. Geol.
Soc. Lond., 90, 159-200.

LEAKE, R.C. and AUCOTT, J.W.   1973.   Geochemical mapping and prospecting by
use of rapid automatic X-ray fluorescence analysis of panned concentrates.
In: Geochemical Exploration 1972.   Institution of Mining and Metallurgy,
London, 389-400.

PLANT, J.   1971.   Orientation studies on stream sediment sampling for a
regional geochemical survey in Northern Scotland.   Trans. Inst. Min.
Metall.,80, B324-B344.

PLANT, J. and RHIND, D.   1974.   Mapping Minerals.   Geogr.Mag., 47, 123-126.

ROBERTS, D.E.   1971.   Structures in the Skiddaw Slates of the Caldew Valley,
Cumberland.   Geol. J ., 7, 225-238.

SHAW, W.T.   1975.   Mining in the Lake Counties., 3rd Edition, Dalesman
Publishing Co. Ltd., Clapham, 128.

SHEPHERD, T.J., BECKINSALE, R.D., RUNDLE, C.C. and DURHAM, J.   1976.
Genesis of the Carrock Fell tungsten deposits.   Trans. Instn. Min.
Metall., 85, B63-B73.
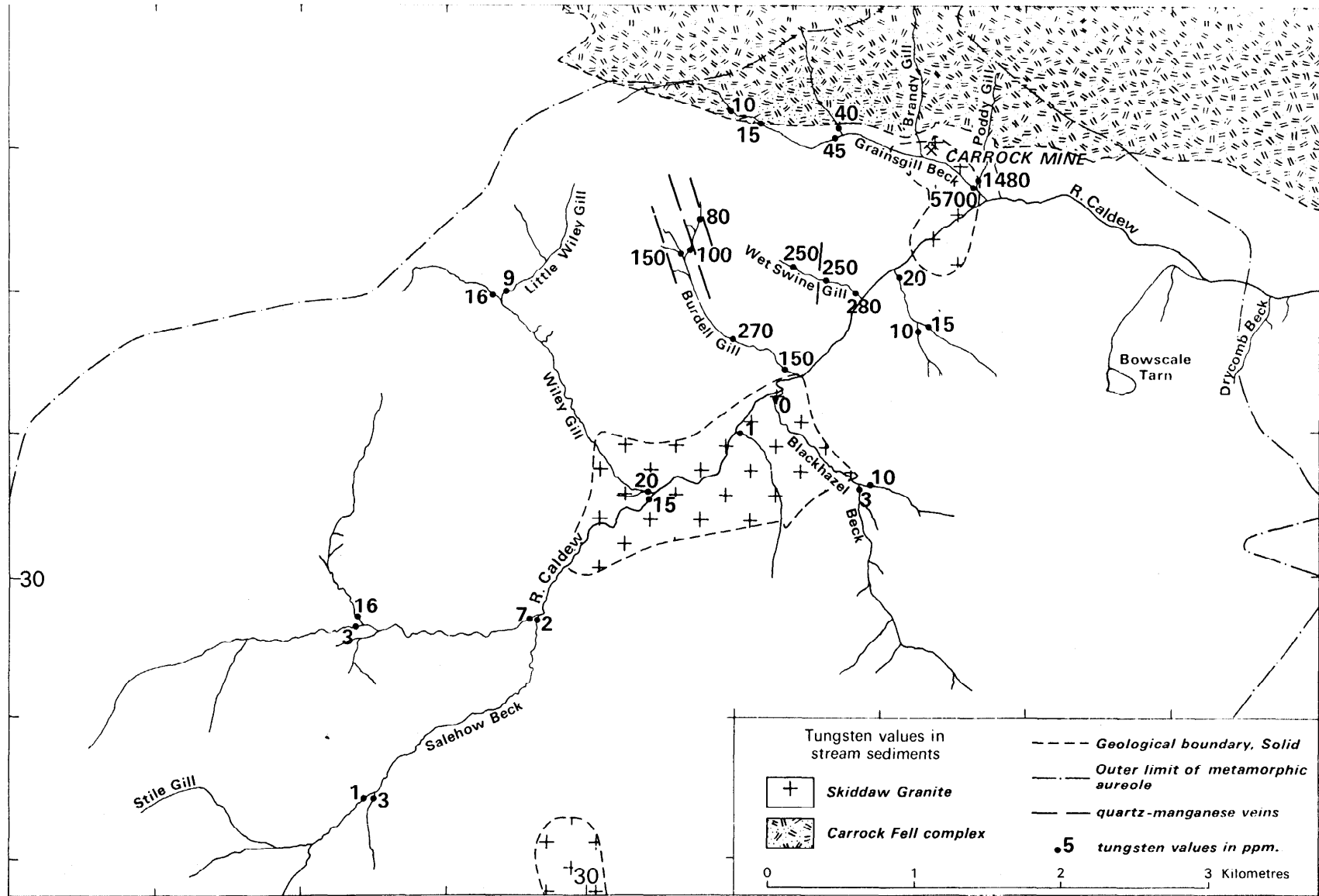
Fig. 3. Tungsten in -100 mesh stream sediments
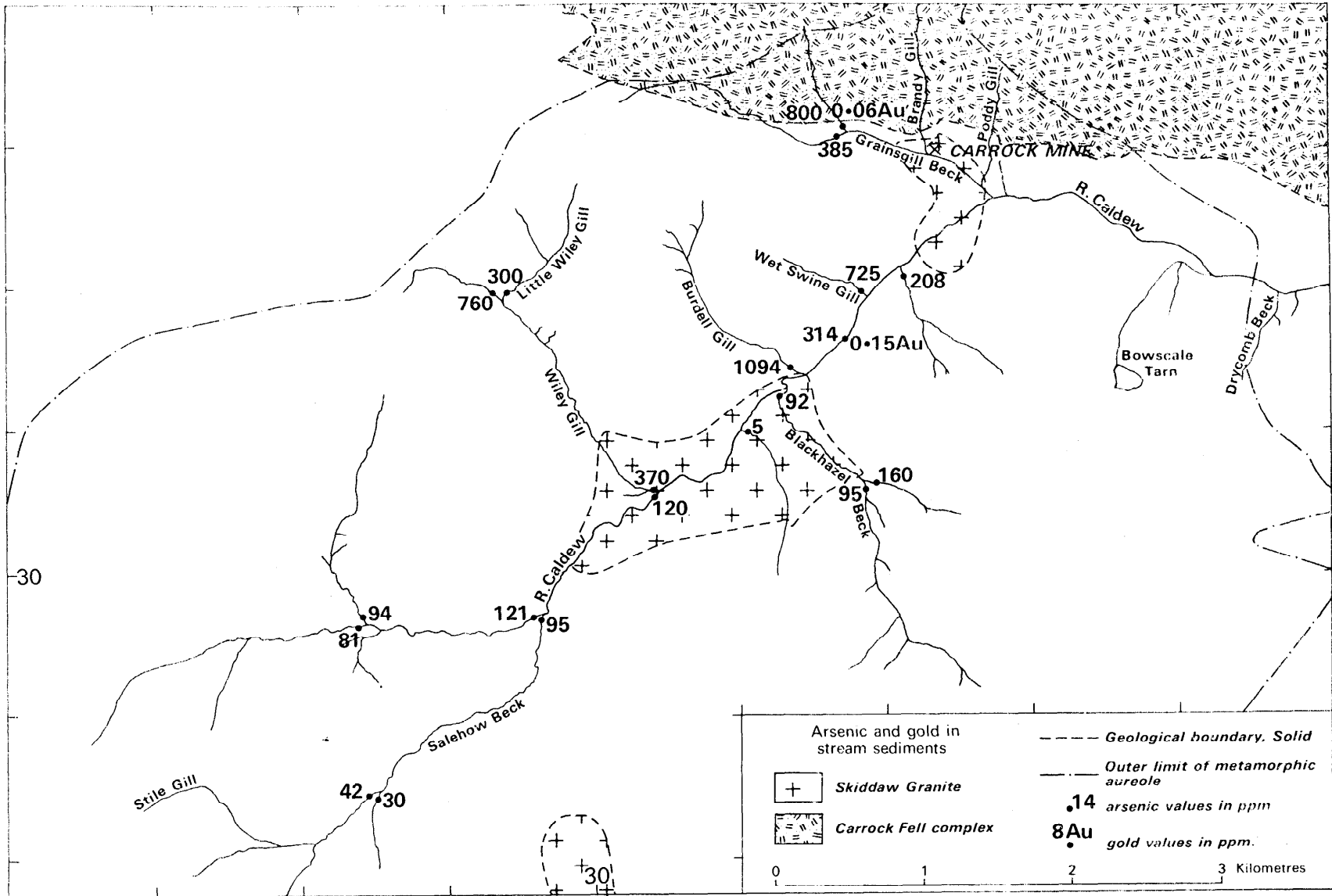
Fig. 4. Arsenic and gold in -100 mesh stream sediments
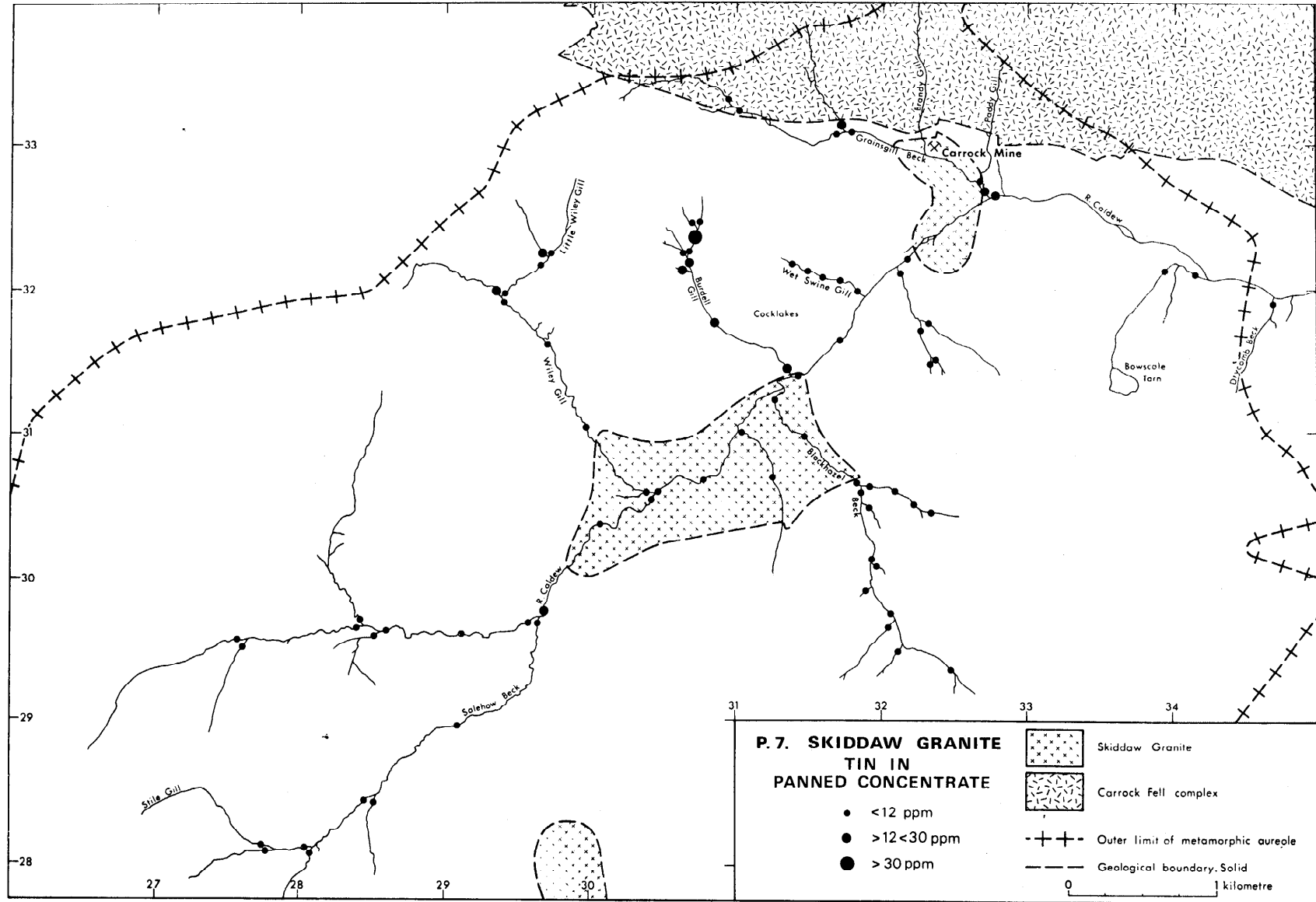
Fig. 5. Tin in panned concentrates
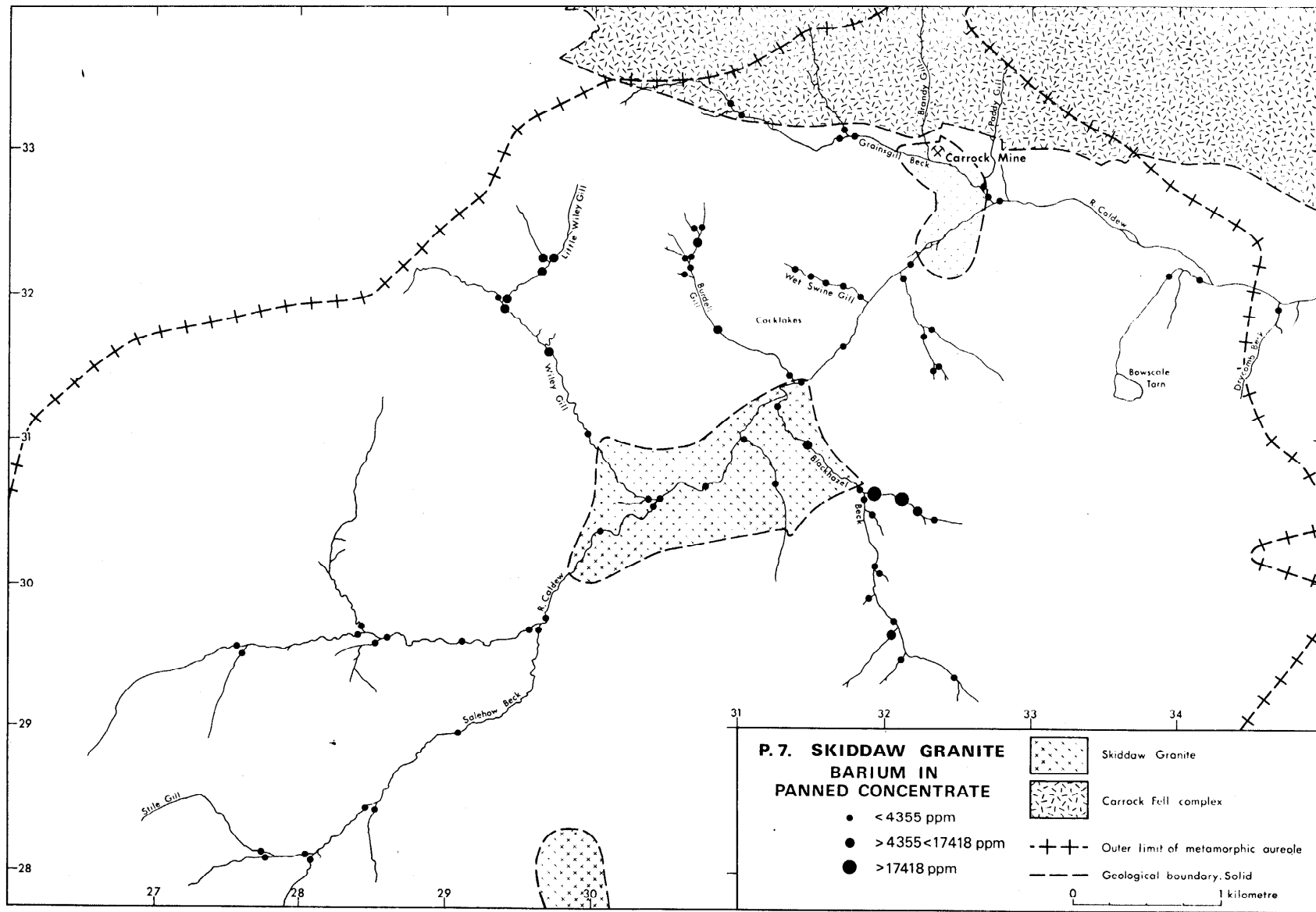
Fig. 6. Barium in panned concentrates
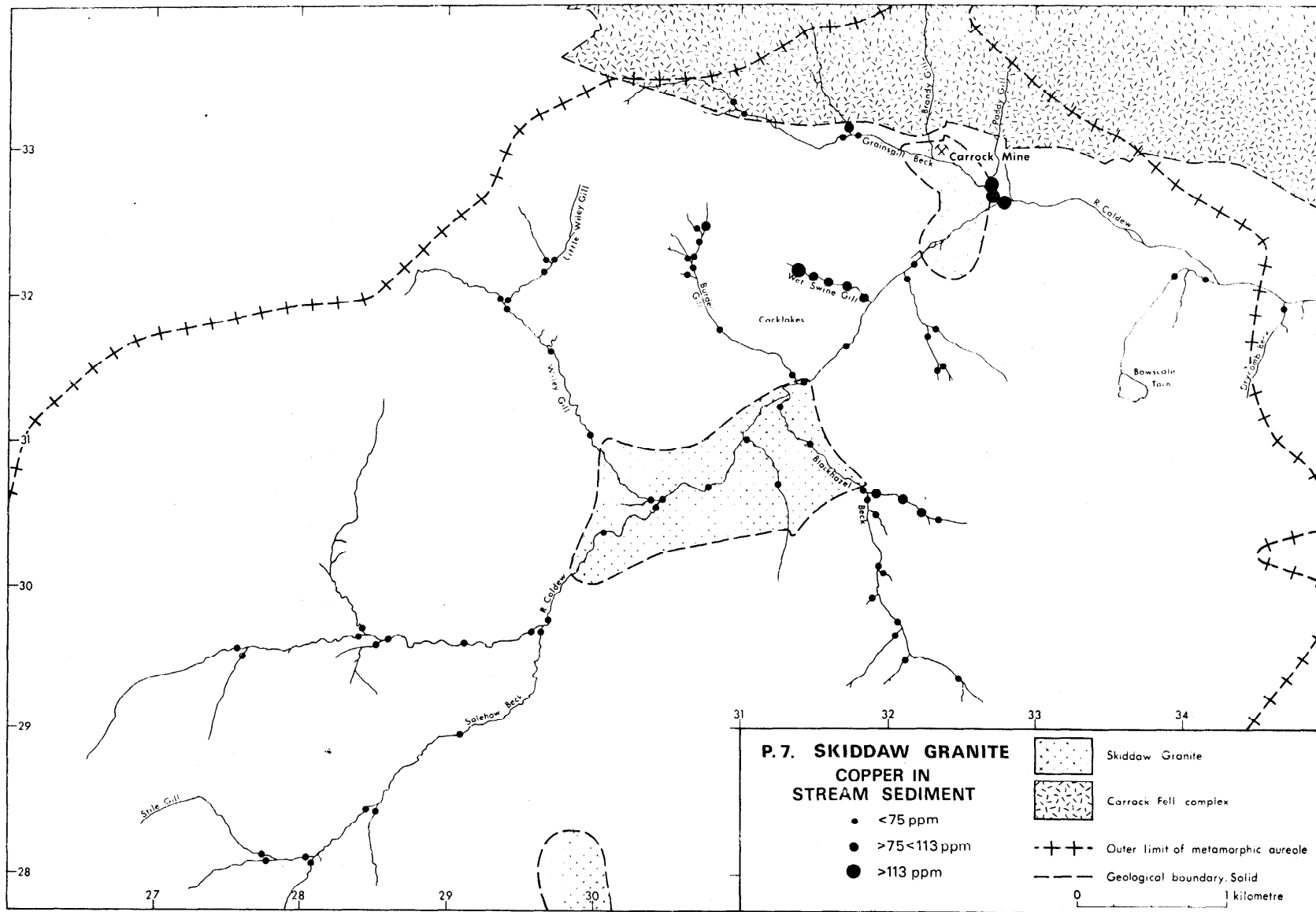
Fig. 7. Copper in -100 mesh stream sediments
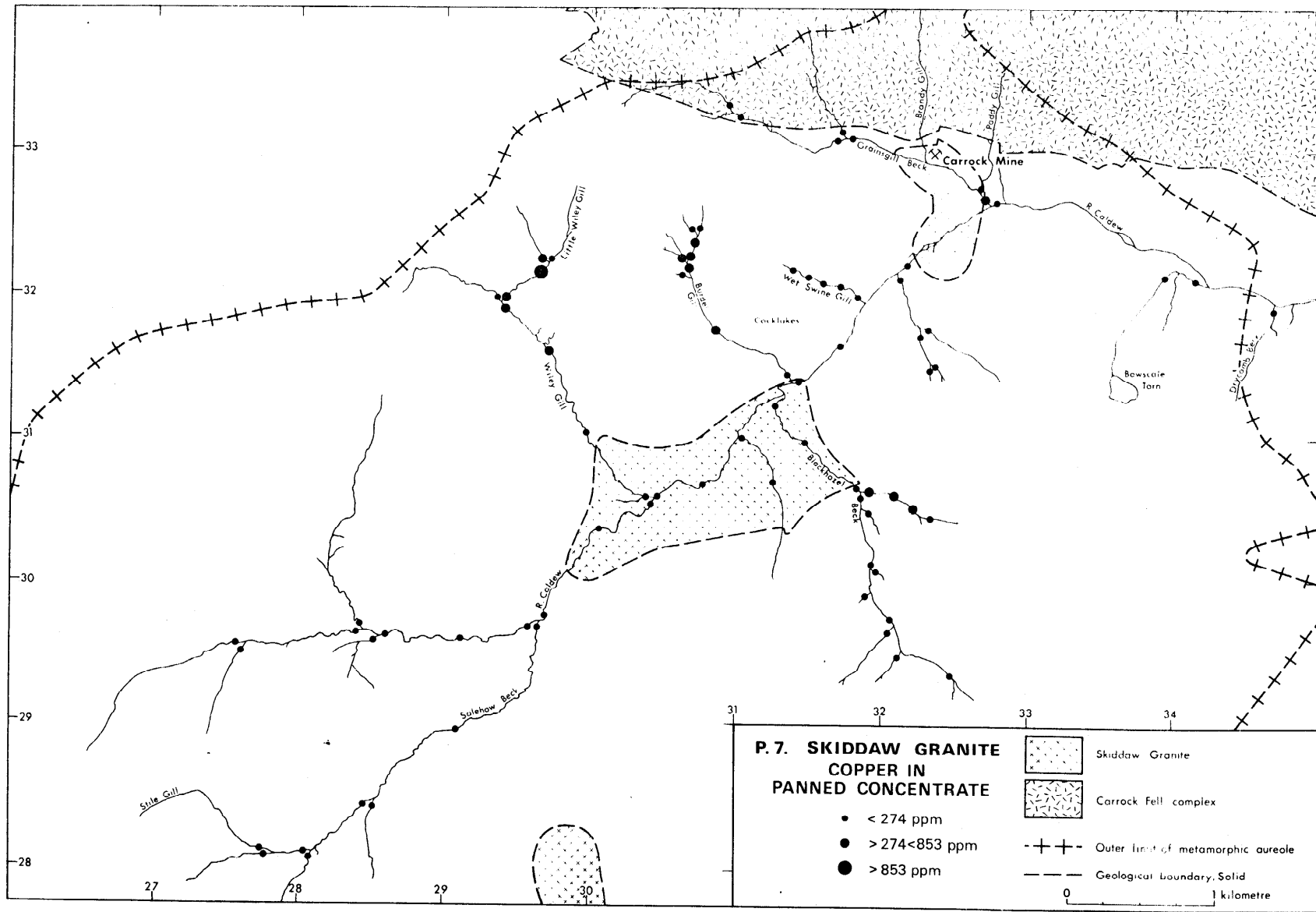
Fig. 8. Copper in panned concentrates

Grainsgill Beck

Carrock Mine

Brandy Gill

Poddy

R. Coldew

Little Wiley Gill

Burdell Gill

Wet Swine Gill

Cocklakes

Bowscale Tarn

Drygill Beck

Wiley Gill

Blackhazel Beck

R. Coldew

Salehow Beck

Stile Gill

P.7. SKIDDAW GRANITE
LEAD IN STREAM SEDIMENT

- • <352 ppm
- • >352<769ppm
- ● >769 ppm

Skiddaw Granite

Carrock Fell complex

- + + - Outer limit of metamorphic aureole

- - - - Geological boundary, Solid

0   1 kilometre

Fig. 9. Lead in -100 mesh stream sediments

P. 7. **SKIDDAW GRANITE**
LEAD IN
PANNED CONCENTRATE

- < 1524 ppm
- > 1524 < 5224 ppm
- > 5224 ppm

Skiddaw Granite

Carrock Fell complex

-+-+- Outer limit of metamorphic aureole

— — — Geological boundary. Solid

0 _____ 1 kilometre
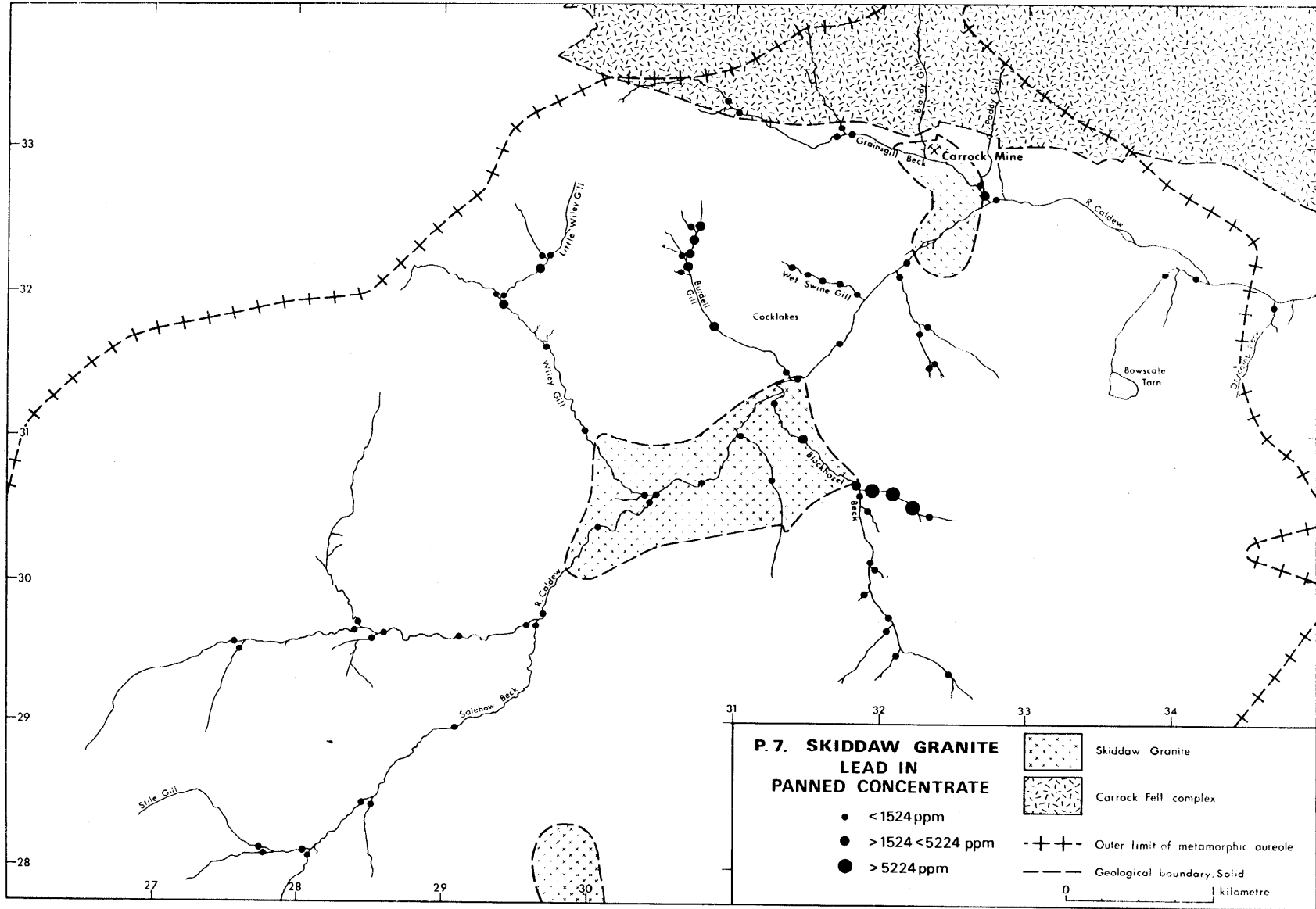
Fig. 10. Lead in panned concentrates
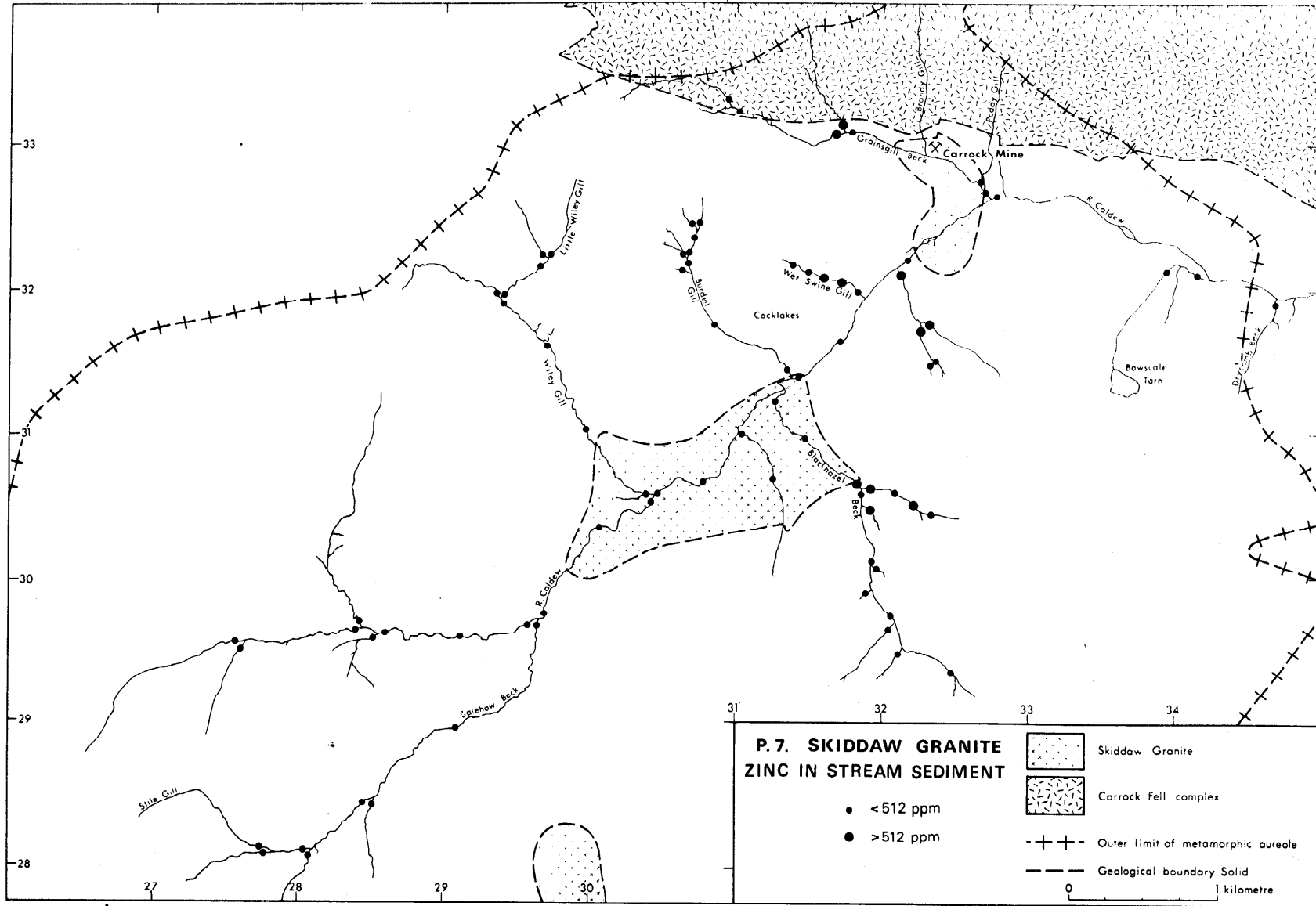
Fig. 11. Zinc in -100 mesh stream sediments

P. 7. SKIDDAW GRANITE
ZINC IN STREAM SEDIMENT

- < 512 ppm
- > 512 ppm

Skiddaw Granite

Carrock Fell complex

- + + - Outer limit of metamorphic aureole

- - - Geological boundary, Solid

0   1 kilometre

21

P. 7. SKIDDAW GRANITE
ZINC IN
PANNED CONCENTRATE

- <750 ppm
- >750 <1722 ppm
- >1722 ppm

Skiddaw Granite

Carrock Fell complex

-+-+- Outer limit of metamorphic aureole

----- Geological boundary. Solid

0   1 kilometre
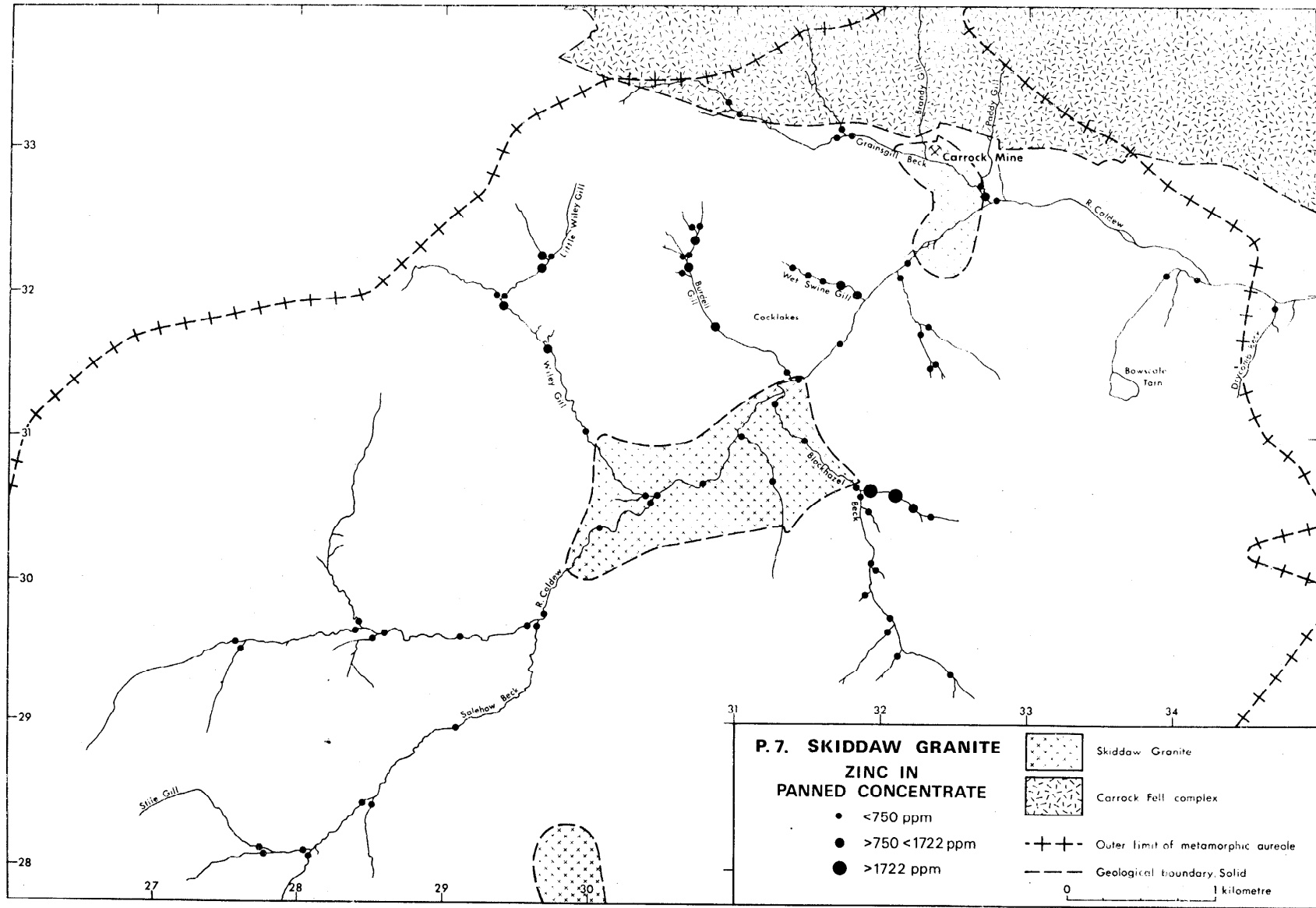
Fig. 12. Zinc in panned concentrates
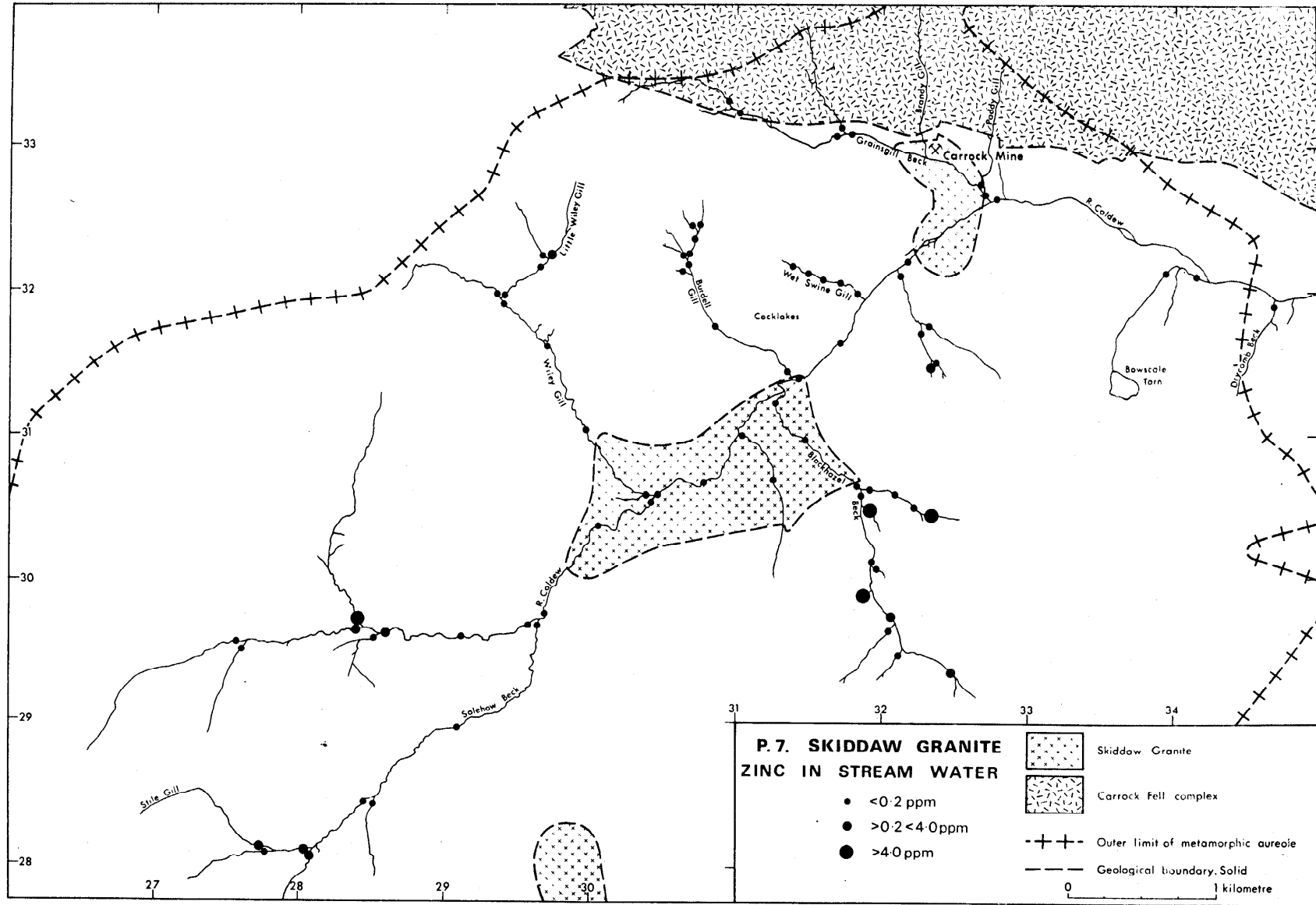
Fig. 13. Zinc in stream waters

Fig. 14. Iron in panned concentrates

P. 7. SKIDDAW GRANITE
IRON IN
PANNED CONCENTRATE

• <15 0 %

● >15 0 %

Skiddaw Granite

Carrock Fell complex

-+ +- Outer limit of metamorphic aureole

— — — Geological boundary. Solid

0   1 kilometre

24
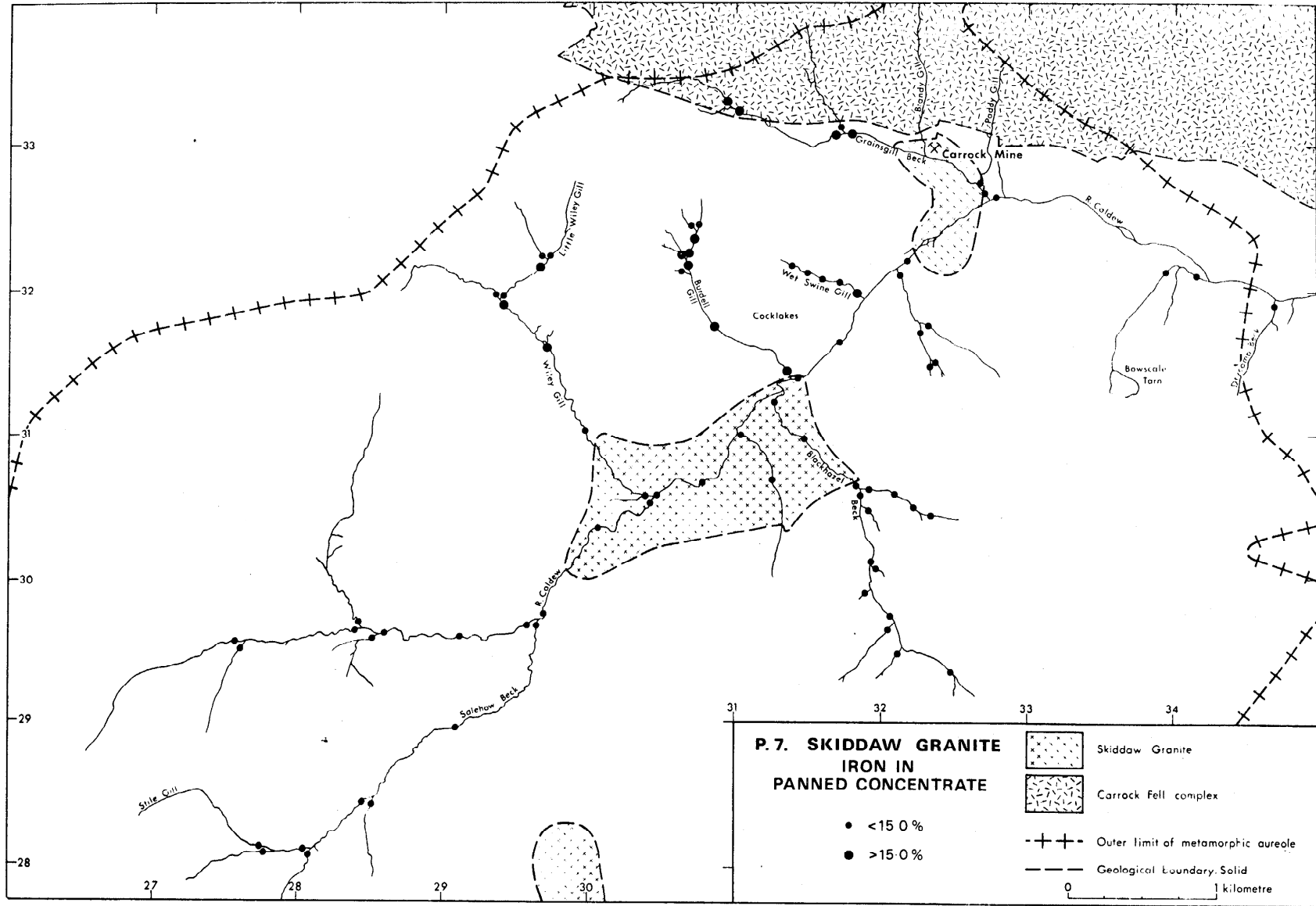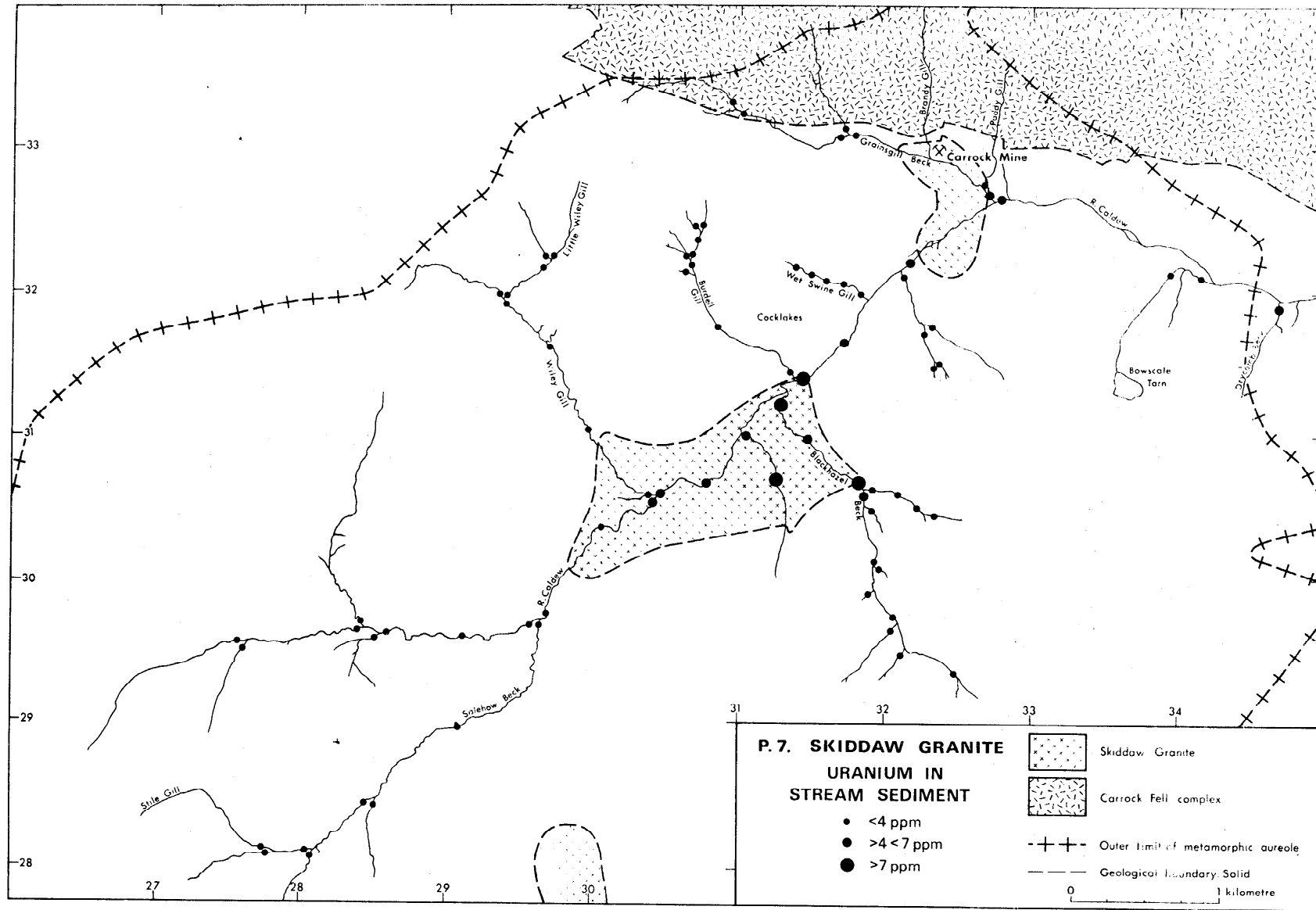
Fig. 15. Uranium in -100 mesh stream sediments

P. 7. SKIDDAW GRANITE

URANIUM IN
STREAM SEDIMENT

- • <4 ppm
- • >4 <7 ppm
- ● >7 ppm

Skiddaw Granite

Carrock Fell complex

–+–+– Outer limit of metamorphic aureole

––––– Geological boundary. Solid

0   1 kilometre

Genesis of Carrock Fell tungsten deposits, Cumbria: fluid inclusion and isotopic study

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Synopsis
Based on a combined fluid inclusion, oxygen isotope and K—Ar age
study of the Carrock Fell tungsten deposits, their genesis and
relationship to the Skiddaw granite are discussed. The results indicate
extensive alteration of the granite soon after emplacement
(390 m.y.) and contemporaneous mineralization by chemically
similar fluids (moderately saline NaCl brines, enriched in tungsten
and periodically charged with CO_2). The data also suggest a
significant interaction between the granite and isotopically light
water of probable non-magmatic origin under the same
pressure—temperature conditions as for the mineralization
(800 bars: 250—300°C). K—Ar ages for coexisting chlorites and
muscovites indicate that chlorite ages are systematically too young,
and do not record the time of mineralization as closely as the
muscovite ages.

A model of ore genesis is presented which is analogous to the
water—rock interaction model proposed for the porphyry coppers.
The implications and recommendations for future exploration in the
area are considered, with particular reference to the tungsten
enrichment in the granite enclosing the zone of known mineral veins.

Location

The Carrock Fell tungsten deposits are located
approximately 2 miles west of Mosedale in the
northeastern part of the Lake District (Fig. 1).
Since their discovery in 1870, mining has been
sporadic, being confined to a group of prominent
veins near the confluence of Grainsgill Beck with
the River Caldew.

Geological setting

Dominating the geological framework of the region
is the Skiddaw granite (Fig. 2). Although poorly
exposed, the granite has an extensive thermal
metamorphic aureole that suggests a partially
unroofed single granite mass at shallow depth. As
illustrated, it intrudes the highly deformed rocks of
the Lower Palaeozoic Skiddaw Slate Series, which
form a continuous northeast—southwest belt across
the northern part of the Lake District. North of
the granite, there is a thick sequence of andesitic
volcanics, originally thought to be equivalent to
the Late Ordovician Borrowdale Volcanic Series,

but now considered to be older.[1] Between these
two formations, and separated from the granite by
only a few hundred feet of metamorphosed slate in
places, is the Carrock Fell gabbro complex. This is
a lensoid mass of gabbros and related granophyric
hybrids elongated parallel to the Caledonian trend
of the adjacent sedimentary rocks. Within this
setting the Carrock Fell tungsten deposits outcrop
in a small area on the northern flank of the
Skiddaw granite.

The north—south-trending veins, which carry
the tungsten ores, traverse the granite, the southern
zone of gabbros and the intervening tract of
metamorphosed slates. The geology of the area is
well documented, with major contributions by
Ward,[2] Harker,[3] Hitchen[4] and Eastwood et al.[5]
Previous accounts of the mineralization have also
been given by Finlayson,[6] Hitchen[4] and Ewart.[7]

Skiddaw granite and associated metasomatism

Despite its apparent size, the Skiddaw granite is
exposed only in three small outcrops (Fig. 2). The
largest is referred to as the 'central' or Caldew
River outcrop, the northernmost as the Grainsgill
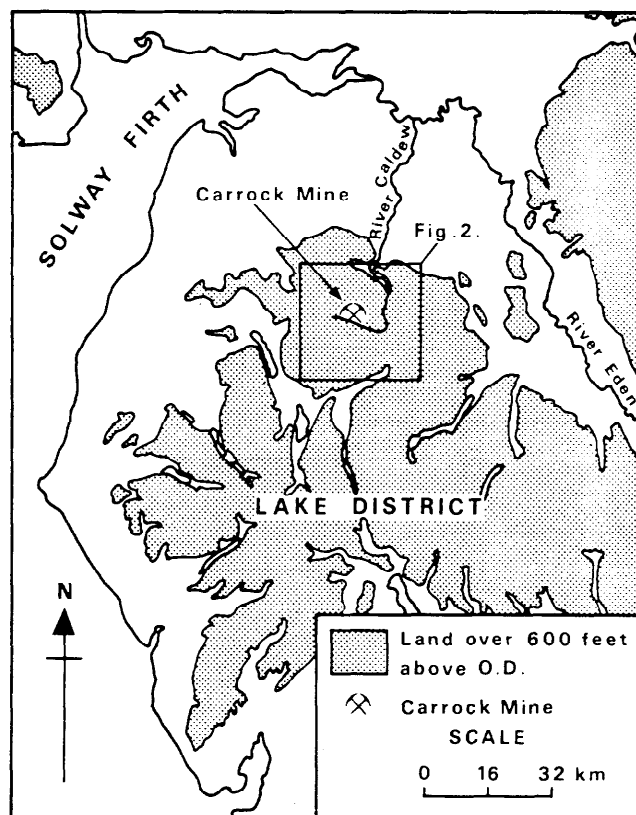
Fig. 1   Geographical location of Carrock Fell area

outcrop, and the southernmost as the Sinen Gill
outcrop. In the Caldew River outcrop, the rock is
mainly a medium-grained biotite granite,
which — apart from weak greisenization and
chloritization — is similar to the biotite
granodiorite of Sinen Gill. From its irregular form,
the Grainsgill outcrop appears to be an elongated
dome with its long axis directed north—south.
Petrographically, the granite is equivalent to that
exposed in the Caldew River, but it differs in
showing a total chloritization of the biotites and
intense replacement of the feldspars by muscovite.
The pervasive 'greisenization' of the granite
culminates in the Grainsgill Beck area, where the
rock is converted to a quartz—muscovite greisen.

Some doubt exists as to the real extent of the Grainsgill greisen; Ewart maintained that it is only developed adjacent to the tungsten-bearing quartz veins. Whatever the boundary between greisen and

with their wallrocks. Though the relative mineral proportions may differ, there is a common paragenetic sequence for all veins.

Early wolframite, scheelite and quartz are
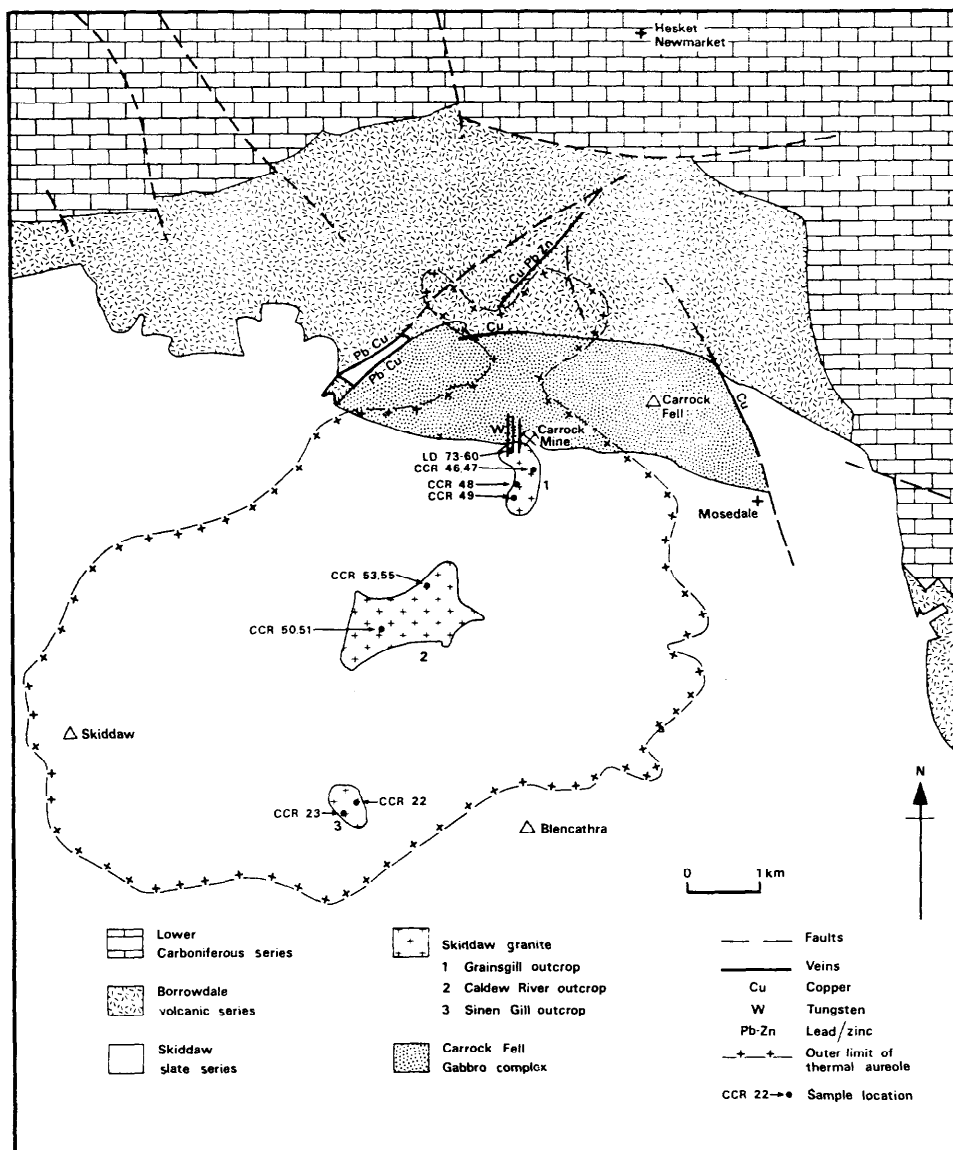
Fig. 2   Geology of Carrock Fell: Skiddaw area with sample locations

greisenized granite, it is clear that there is substantially less alteration in the Caldew River area than in the Grainsgill outcrop, but appreciably more than at Sinen Gill.

Mineralization

The known mineralized ground is confined to the northern margin of the Skiddaw granite and characterized by a series of steeply dipping north—south quartz veins, particularly along Grainsgill Beck (Fig. 3). The largest of these veins have been worked from Carrock mine and are, from east to west, the Smith, Harding and Emmerson veins. Quartz is the dominant mineral, with lesser amounts of wolframite, scheelite, arsenopyrite, pyrite, pyrrhotite, sphalerite and ankerite in general order of decreasing importance. Other minerals recorded include molybdenite, chalcopyrite, bismuthinite, apatite, dolomite, calcite, barites and muscovite. Work by Finlayson,[6] Hitchen[4] and Ewart[7] has shown that the veins vary from 0.1 to 1.5 m in width and have sharp contacts

succeeded by Fe—As—Cu—Zn sulphides, which, in turn, are followed by barren quartz with minor carbonates and muscovite. Clusters of tabular wolframite crystals on or near the vein walls are characteristic features of the deposits. The quartz is massive throughout and shows no evidence for major breaks in deposition.

Wallrock alteration is minimal, and conspicuous only in the granite where the rock is converted to a quartz—muscovite greisen carrying minor arsenopyrite, pyrite and apatite. This is very similar to that described by Hall[8] for quartz—wolframite—cassiterite veins in the Cligga Head area, Cornwall. In the gabbro and hornfels, the alteration is slightly modified compared with that in the granite, owing to differences in bulk chemistry.[5] Except for small east—west cross fractures carrying quartz, galena and sphalerite, there is no significant post-ore displacement on the veins. The cross fractures are regarded as equivalents of the larger east—west-trending lead—zinc veins of the Caldbeck Fell system further north.

Sampling

To investigate the nature of the ore fluids and genetic relationship between magmatism, greisenization and mineralization in the Carrock—Skiddaw area, representative samples were taken of the granite, greisen and mineral veins. These provided the basis for fluid inclusion, oxygen isotope, potassium—argon and tungsten analysis. As Fig. 2 shows, all three outcrops of the Skiddaw granite were included, giving a complete sequence through the zone of metasomatic alteration. For the fluid inclusion and oxygen isotope studies carefully located *in-situ* samples of quartz gangue were collected from development levels in Carrock mine where Harding vein intersects the gabbro complex (Fig. 4). Because of the relatively simple mineral paragenesis, samples were classified either as 'mineralized' quartz (early quartz with associated wolframite, scheelite and/or sulphides) or 'barren' quartz (late quartz with associated carbonates and muscovite).

Analytical methods

Thermometric analysis of the fluid inclusions was carried out on polished quartz slices 1 mm thick; electrolytically cleaned duplicates were used for subsequent chemical analysis. Aqueous extracts of the inclusion fluids were analysed as follows: Cl^-, Br^-, I^- by neutron activation analysis; Ca^{++}, Mg^{++}, Na^+, K^+ by atomic absorption and emission spectrophotometry; and SO_4^{--} by X-ray fluorescence analysis. Conventional methods were used for determining the $\delta^{18}O$ values and K—Ar ages. Mineral separates were prepared from whole rock samples by serial heavy liquid and electromagnetic separation. For the tungsten determinations a modified colorimetric technique based on the zinc dithiol method was used.[9]

Fluid inclusion studies

The vein quartz, without exception, contains an abundance of two-phase fluid inclusions consisting of a liquid phase and complementary vapour phase; the latter occupies less than 25% of the total volume. They average 10—30 μm in diameter, are ovoid or multifaceted in form, and occur in both isolated non-planar groups and discontinuous intersecting planar arrays. Since they show no obvious relationship to growth zones or crosscutting secondary fractures, the inclusions are considered collectively as pseudo-secondaries (i.e. formed during crystal growth). In one sample of 'mineralized' quartz (F.I. 209), however, a second type of inclusion occurs, which contains liquid CO_2 at room temperature. The wedge-like equant shape of these inclusions does not allow exact phase proportions to be calculated, but an approximation — aqueous liquid/liquid CO_2/gaseous CO_2 : 40/30/30 — may be considered typical. On warming to 26°C, the CO_2 undergoes partial homogenization into the liquid state. No daughter minerals were observed in either type of inclusion.

The selection of individual inclusions for thermometric analysis was made difficult by the high degree of post-depositional 'necking'. In extreme cases a complete separation of the liquid and vapour phases had occurred. When such inclusions are used it is important to distinguish between coexisting high- and low-vapour types due to fluid boiling and the anomalous coexistence caused by necking. In this instance the absence of a vapour bubble in the liquid portion of the 'necked' inclusions at room temperature was not consistent with boiling at +200°C.

Homogenization temperatures for the vein quartz, as shown in Fig. 5, indicate a small but significant temperature difference between the mineralized and barren stages of quartz deposition. This suggests a relatively constant temperature during vein formation, with only a slight decrease after the early deposition of wolframite, etc.
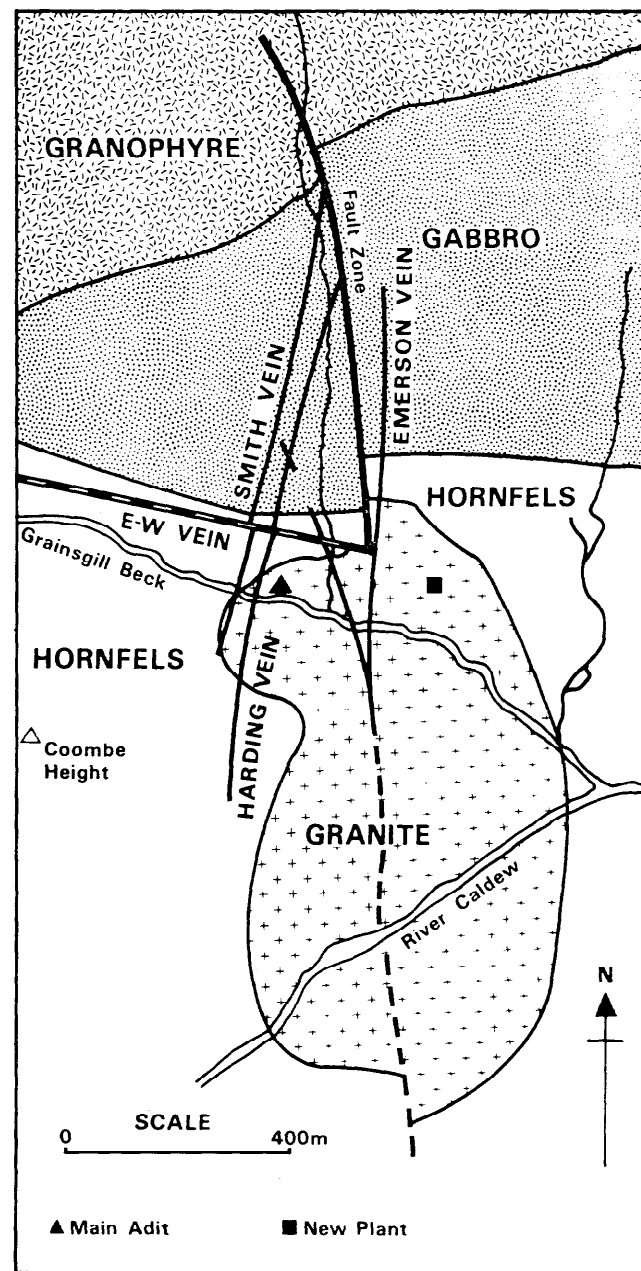
Fig. 3   Simplified geology of Carrock mine area

Positive skewing of the 'barren' quartz population due to the incorporation of material intermediate in character provides a somewhat qualitative confirmation of this suggestion. The persistence of stable thermal conditions would greatly facilitate changes in inclusion morphology in response to local thermal gradients, thereby accounting for the high degree of necking.

Estimates of the gross salinity of the ore fluids obtained from freezing measurements on selected

inclusions indicate no systematic change during mineralization (Fig. 5). Expressed as equivalent wt% of NaCl, values range from 6.8 to 9.6, with a mean of 8.3. Chemical analyses of the aqueous

correspond closely with the deposition of K-mica and Ca carbonates during the final stages of mineralization.

Because homogenization temperatures record
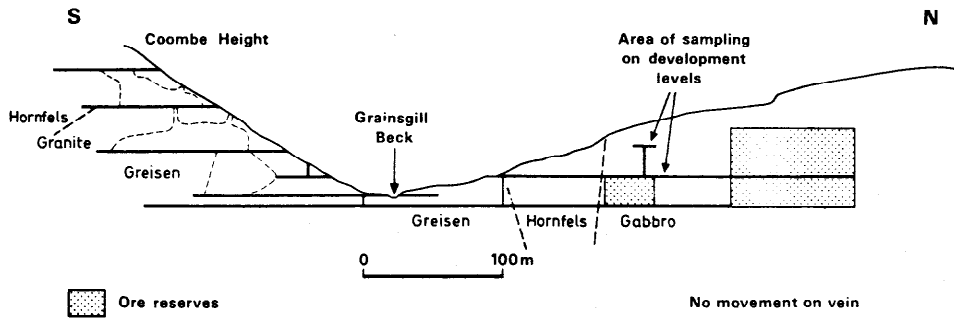
Fig. 4   Section along Harding vein, Carrock mine, showing levels and area of sampling

extracts from crushed material demonstrate that the liquid phase of the two-phase inclusions is essentially a NaCl brine. Variation in the minor components reveals, however, that subtle chemical changes were occurring in the source area which correlate with recognizable changes in mineral deposition (Table 1). Decreases in Na/K and Na/Ca

only the minimum temperature of mineral formation, it is necessary to apply a pressure correction to obtain the actual temperature at the time of trapping. Unfortunately, there is insufficient geological information from which to estimate the hydrostatic or lithostatic pressures for the Carrock Fell area by reconstruction of the

(Note: Temperatures are uncorrected for pressure)
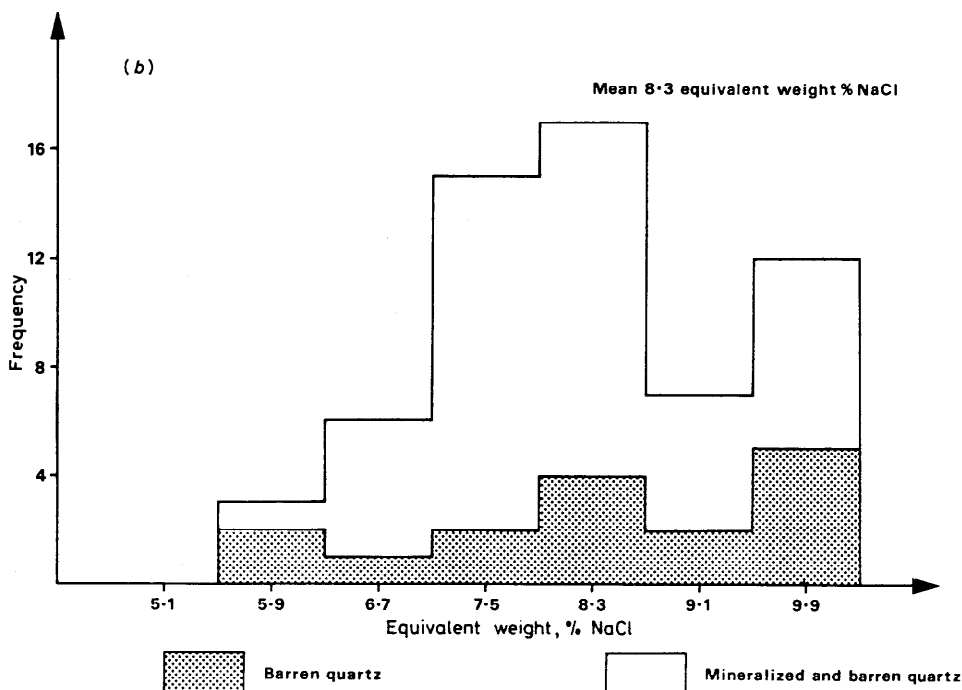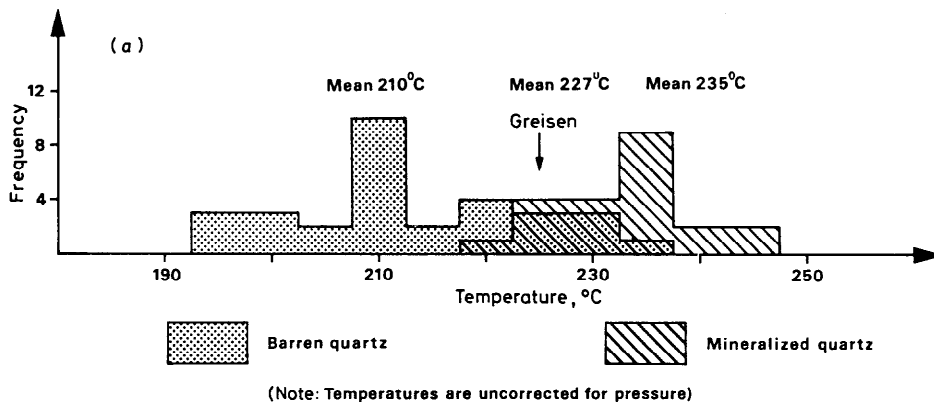
Fig. 5   Frequency distribution graphs for (a) homogenization temperatures and (b) salinity of pseudo-secondary inclusions in quartz 'Harding vein', Carrock mine

Table 1 Chemistry of inclusion fluids in quartz from Harding vein, Carrock mine

Sample number	Material	Atomic ratios				
		Na/K	Cl/Br	Ca/Mg	Na/Ca	Cl/SO$_4$
F.I. 203		>104*	154	6.0	8.7	25
F.I. 209	Mineralized	60	69	<0.3†	>30†	>25§
F.I. 210	quartz	17	176	0.3	>43†	>25§
F.I. 211		>114*	110	– ‡	>57†	>25§
F.I. 204		23	556	1.3	5	34
F.I. 205		11	232	0.8	13	25
F.I. 207	Barren quartz	23	77	2.7	7	>25§
F.I. 208		46	444	2.3	13	>25§

Summary of fluid chemistry

Atomic ratios	Barren quartz	Mineralized quartz
Na/K	26	> 74
Cl/Br	327	124
Ca/Mg	1.8	< 2.2**
Na/Ca	10	> 35
Cl/SO$_4$	>27	> 25

Ratios refer to analyses of aqueous leachates of inclusion fluids:
* below detection limit for potassium; † below detection limit for calcium; ‡ no magnesium determination made; § below detection limit for sulphate; ** severely biased by ratio for F.I. 203

superimcumbent load, but a value for the minimum pressure can be derived from the theoretical work of Haas[10] on the density of vapour-saturated NaCl–H$_2$O solutions. At 240°C, for a 10 wt% NaCl solution the minimum pressure required to prevent boiling is 31 bars. This is equivalent to a hydrostatic head of 327 m, and gives a corresponding minimum pressure correction of <5°C. An alternative method, which provides a better estimate of the actual pressure, is the use of complex liquid CO$_2$ inclusions. It is assumed that

inclusions of this type have formed from a heterogeneous H$_2$O–CO$_2$ solution owing to the restricted mutual solubility below the critical region in the system H$_2$O–CO$_2$; the excess CO$_2$ forms a separate liquid phase in equilibrium with the aqueous phase. To apply the relevant thermodynamic data, one requires inclusions that have trapped only one phase. The restricted occurrence of these inclusions in the vein quartz severely limits the application of this method to the Carrock Fell deposits: values for the pressure must be regarded as semi-quantitative. Assuming simultaneous trapping, the partial homogenization temperatures for F.I. 209, together with the data of Vukalovich and Altunin[11] and of Kennedy,[12] and the mean homogenization temperatures for coexisting two-phase aqueous inclusions, give a pressure of ~800 bars. According to Lemmlein and Klevtsov,[13] this is equivalent to a pressure correction of +60°C for a NaCl solution of 10 wt%. Thus, the true temperature for the 'mineralized' quartz and, hence, the estimated depositional temperature of the wolframite is 295°C, and that for the 'barren' quartz is 275°C. The apparently large molar volume of H$_2$O in the liquid CO$_2$ inclusions is consistent with the observed mutual solubility for the estimated P–T conditions.[14,15]

If the apparent pressure of 800 bars is entirely hydrostatic, the corresponding lithostatic loading on the country rocks is 2 kb, assuming a density of 2.5 g/cm^3. This value is less than the minimum pressure given by Fyfe[16] for the kyanite–sillimanite–andalusite triple point, and is consistent with the development of andalusite in the outer thermal metamorphic aureole of the granite.

A less detailed study of the Grainsgill greisen proved the existence of identical two-phase (liquid/vapour) inclusions in quartz grains intergrown with metasomatic muscovite. Assuming no substantial difference in pressure, the corrected

Table 2 δ^{18}O of Harding vein quartz (per mil)

Sample number	Quartz type	Measured δ^{18}O	Calculated* δ^{18}O of fluid in equilibrium at			
			215°C†	235°C†	275°C‡	295°C‡
F.I. 203		12.78		+ 1.68		+ 4.44
F.I. 209		12.58		+ 1.48		+ 4.24
F.I. 210	Mineralized quartz	13.16		+ 2.06		+ 4.82
F.I. 211		12.40		+ 1.30		+ 4.06
		a.m 12.91		a.m + 1.63		a.m. + 4.39
F.I. 204		13.28	+ 1.02		+ 4.12	
F.I. 205		13.30	+ 1.04		+ 4.14	
F.I. 207	Barren quartz	12.29	+ 0.03		+ 3.13	
F.I. 208		12.78	+ 0.52		+ 3.62	
		a.m. 12.73	a.m + 0.65		a.m + 3.75	

* Calculated from the following equation (from O'Neil et al.[34]): $10^3 \ln\alpha = -2.73 + 3.57 (10^6 \, T^{-2})$
† Mean homogenization temperatures (uncorrected).
‡ Mean homogenization temperatures (corrected for pressure).

temperature of greisenization given by the mean homogenization temperature is 287°C.

Oxygen isotopic studies

Oxygen isotope analyses were made of vein quartz from the Harding lode and mica separates from the Skiddaw granite and Grainsgill greisen. By use of the measured $\delta^{18}O$ values for the vein quartz in

Independent estimates of the temperature of greisenization given by the oxygen isotopic fractionation between muscovite and chlorite for LD-CCR 46, 48 and 49 are comparable to the mean pressure-corrected inclusion temperature for the greisen (Table 3). The apparent spread in values (250–300°C) probably reflects a combination of isotopic disequilibrium, thermal variation within

Table 3 $\delta^{18}O$ of minerals from Skiddaw granite and Grainsgill greisen (per mil)

Locality	Sample number	Rock type	Mineral	Measured $\delta^{18}O$ (average)	ΔMuscovite – chlorite	Calculated* temperature, °C
Sinen Gill	CCR-22	Granite	Biotite	+ 6.75		
	CCR-23	Granite	Biotite	+ 6.83		
Caldew River	CCR-50	Granite	Biotite	+ 6.04		
	CCR-51	Granite	Biotite	+ 5.90		
	CCR-53	Granite	Biotite	+ 6.32		
	CCR-55	Granite	Biotite	+ 6.15		
Grainsgill	CCR-46	Granite	Chlorite	+ 6.14 (+ 5.65) †	3.90	241 ± 20
	CCR-46	(Greisenized)	Muscovite	+ 9.55		
	CCR-47	(Greisenized)	Chlorite	+ 7.58 (+ 7.08)†	2.50	425 ± 40
	CCR-47	(Greisenized)	Muscovite	+ 9.58		
	CCR-48	(Greisenized)	Chlorite	+ 6.41 (+ 5.92)†	3.33	296 ± 20
	CCR-48	(Greisenized)	Muscovite	+ 9.25		
	CCR-49	(Greisenized)	Chlorite	+ 7.37 (+ 5.97)†	3.69	260 ± 20
	CCR-49	(Greisenized)	Muscovite	+ 9.66		
	LD 73–60	Greisen	Muscovite	+ 9.99		

Summary
Sinen Gill biotites   av. $\delta^{18}O$ + 6.79‰   (range + 6.75 to + 6.83)
Caldew River biotites   av. $\delta^{18}O$ + 6.10‰   (range + 5.90 to + 6.32)
Grainsgill muscovites   av. $\delta^{18}O$ + 9.51‰   (range + 9.25 to + 9.66)
Grainsgill chlorites   av. $\delta^{18}O$ + 6.16‰   (range + 5.65 to + 7.08)

*Calculated by use of equation derived from O'Neil and Taylor,[35] O'Neil et al.,[34] and Wenner and Taylor:[36]

$$10^3 \ln\alpha = + 0.80 + 0.82 (10^6 T^{-2})$$

† Values corrected for muscovite contamination.

conjunction with the inclusion homogenization temperatures, $\delta^{18}O$ values may be derived for the ore fluid. As shown in Table 2, though the respective values for the 'mineralized' and 'barren' quartz groups are not significantly different, they suggest the involvement of a relatively light fluid during mineralization. Similarly, the $\delta^{18}O$ values for the whole rock micas (Table 3) demonstrate the role of isotopically light water in the evolution of the granite–greisen system. For biotites from the Sinen Gill and Caldew River outcrops the $\delta^{18}O$ values fall within the general range of normal igneous biotites (5–7‰).[18] Closer examination suggests, however, a superimposed sympathetic relationship between $\delta^{18}O$ and potassium content (Table 4). The progressive depletion in ^{18}O is interpreted as a function of increasing chloritization peripheral to the main area of greisenization by relatively light water.

the Grainsgill outcrop and analytical error. Except for possible contamination by primary muscovite,[4] no geological explanation can be given for the highly anomalous value for CCR-47.

Potassium–argon studies

Potassium–argon ages were determined on hydrothermal muscovites from the Harding lode

Table 4   Sympathetic relationship between $\delta^{18}O$ and K content of Skiddaw granite biotites

Sample number	Mean $\delta^{18}O$, ‰	Mean K content, wt %
CCR-50, CCR-51	+ 5.97	4.090
CCR-53, CCR-55	+ 6.24	6.430
CCR-22, CCR-23	+ 6.75	7.030

and mica separates from the Skiddaw granite and Grainsgill greisen. As shown in Table 5, replicate biotites from Sinen Gill give concordant ages within the limits of experimental error, and agree with the value of 399 ± 6 m.y. previously published by Brown and co-workers.[19] Since the area is well beyond the zone of greisenization, and there is only slight chloritization of the biotites, it is suggested that the mean age of 392±4 m.y. be taken as the final cooling of the granite. For the vein muscovites, the corresponding mean age of 387 ± 4 m.y. is not significantly different, suggesting a close temporal relationship between the cooling of the granite through the blocking temperature for ^{40}Ar diffusion in biotite and mineralization.[20]

The increasing degree of metasomatic alteration in the Caldew River outcrop, represented by a progressive chloritization of the biotites, is accompanied by an inverse relationship between K content and age. Sample CCR-50 with only 2.7% K gives an apparent age of 419 m.y.; CCR-53 and CCR-55 with more normal K contents yield values similar to those of the unaltered Sinen Gill biotites. In view of the lack of evidence for excess argon, it must be assumed in this case that preferential K loss occurred during chloritization. This is contrary to the experimental studies of leaching carried out by Kulp and Engels,[21] but is in accord with later work by Evernden and Kistler,[22] who attributed the phenomenon to the presence of argon atoms impelled into more retentive non-potassium lattice sites by recoil during radioactive decay. Chlorites from the Grainsgill outcrop, within the zone of weak greisenization, show a wide spread of apparent ages (337—393 m.y.). Except for minor muscovite contamination, the chlorite separates showed no detectable mineralogical differences between samples. Contamination was greatest for chlorite CCR-49, as verified by the potassium analyses for the standard and ultrapure mineral

Table 5   K—Ar ages on minerals from Skiddaw granite and Carrock mine (Harding vein)

Locality	Sample number	Mineral	K—Ar ref	% K	Vol Rg ^{40}Ar (nl/g at NTP)	% Atm ^{40}Ar	Age (m.y.)
Sinen Gill	CCR-22	Biotite	75/76	7.054	123.14	5.88	393 ± 6
	CCR-23	Biotite	75/77	7.001	121.54	8.17	391 ± 6
Caldew River	CCR-50	Biotite	75/78	2.669	49.96	9.46	419 ± 8
	CCR-51	Biotite	75/79	5.516	97.47	5.58	398 ± 6
	CCR-53	Biotite	75/80	6.345	107.94	4.87	384 ± 6
	CCR-55	Biotite	75/81	6.509	108.39	3.15	377 ± 6
Grainsgill	CCR-46	Muscovite	75/82	8.169	137.32	6.72	380 ± 6
		Chlorite	75/83	1.119	17.34	15.87	353 ± 11
	CCR-47	Muscovite	75/84	7.808	128.97	5.92	374 ± 6
		Chlorite	75/85	1.552	22.87	8.07	337 ± 5
	CCR-48	Muscovite	75/86	7.998	136.96	4.16	387 ± 6
		Chlorite	75/87	1.174	20.49	16.58	393 ± 6
		Chlorite*	75/101	0.244	3.942	59.23	366 ± 8
	CCR-49	Muscovite	75/88	7.509	125.82	2.50	379 ± 6
		Chlorite	75/89	2.870	46.50	8.85	368 ± 6
		Chlorite*	75/102	0.208	3.174	32.72	348 ± 6
Grainsgill (greisen)	LD 73—60	Muscovite	75/90	9.068	153.29	5.62	382 ± 6
Carrock mine (Harding vein)	Adit level	Muscovite	75/91	9.001	153.92	2.68	386 ± 6
	No. 3 level	Muscovite	75/92	8.842	152.14	2.46	388 ± 6

* Chlorite free from muscovite contamination.
Constants used in age calculations: λ^e = 0.584 x 10^{-10} yr^{-1}
λ^β = 4.72 x 10^{-10} yr^{-1}
^{40}K/K = 0.0119 at %
Errors are quoted at the one-sigma level and are estimates of analytical precision only. They do not incorporate errors due to argon loss, excess argon or errors in the decay constants.

concentrates (Table 5). It would appear, therefore, that the chlorites have undergone variable argon loss, and are unsuitable for precise K—Ar dating. By contrast, the coexisting muscovites, together with the muscovite from the Grainsgill greisen, give concordant ages. Excluding samples diluted by chlorite (CCR—47 and CCR—49), the mean age for the greisenization is estimated as 383 ± 4 m.y.

Tungsten geochemistry

Though the fluid inclusion and oxygen isotopic data provide an insight into the nature of the ore fluids, they do not resolve the more intractable problem of identifying the source of the tungsten. In view of the intimate relationship between greisenization and mineralization, one of two possible hypotheses may be correct: either

Table 6   Tungsten analyses for Skiddaw granite and Grainsgill greisen (whole rocks)

Locality	Sample number	Material	Tungsten, ppm
Sinen Gill	CCR-22	Granite	<1
	CCR-23		<1
Caldew River	CCR-50	Granite	<1
	CCR-51		<1
	CCR-53		1
	CCR-55		<1
Grainsgill	CCR-46	Greisenized granite	2
	CCR-47		3
	CCR-48		2
	CCR-49		4
	LD 73—60	Greisen	15

tungsten is released from the granite during chloritization and greisenization as a result of water—rock interaction, or tungsten is introduced into the mineralized areas from outside the system. Whole rock analyses for tungsten, as given in Table 6, tend to support the second model; the gradual increase from 1 ppm of W in Sinen Gill to 15 ppm of W in Grainsgill suggests a definite external source. Analyses for the separate mica phases (Table 7) also indicate a preferential concentration of tungsten in the muscovite fraction. Thus in the absence of other tungsten-bearing minerals the spatial variation in tungsten can be explained by the development of metasomatic muscovite.* To account for the observed magnitude of the geochemical anomaly by this process demands that the fluids were initially enriched in tungsten.

Unlike the latter model, the former is internally constrained and depends on a concomitant release of tungsten from the Skiddaw granite during alteration. From data by Ivanova,[23] the biotites of biotite granites associated with W—Sn mineralization carry most of the available metal (5 ppm W). Values for the Skiddaw granite are comparable, but no amount of redistribution can explain the apparent increase in tungsten in the altered granite. To maintain this model would
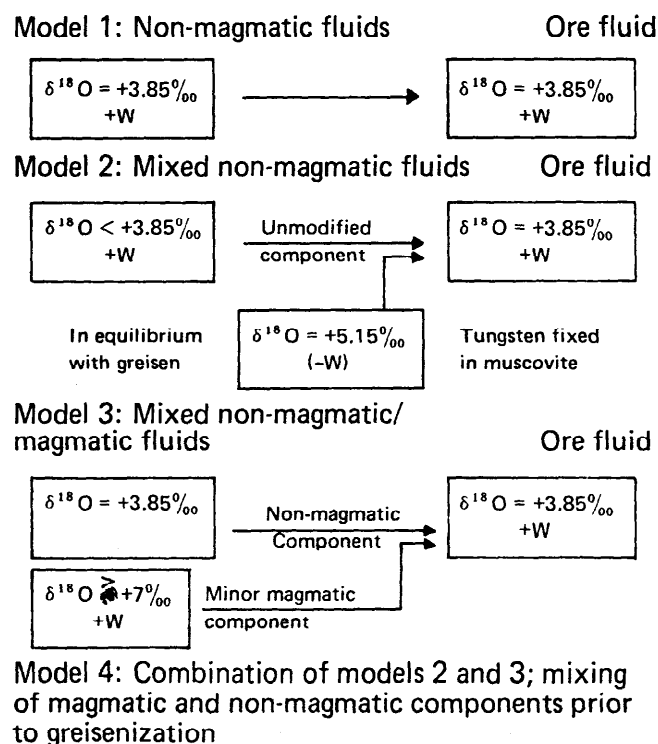
* Examination of the heavy mineral concentrates confirmed the absence of other tungsten mineral, except in the greisen, where accessory wolframite and scheelite were identified.

require a substantial depletion in unexposed or deeper levels of the granite followed by a relative enrichment in areas proximal to the veins.

If, as the evidence suggests, the tungsten has been introduced into the granite, theories regarding its ultimate source must remain speculative and unproven.

Discussion

Good agreement between the fluid inclusion and oxygen isotope data strongly supports the hypothesis for a genetic link between mineralization and alteration of the granite. This is most convincingly demonstrated by the estimated temperatures of mineral deposition (265—95°C) and greisenization (240—95°C), and the calculated $\delta^{18}O$ for the ore fluids (+3—5‰) and fluid in equilibrium with the greisenized granite (+4—6‰). Further substantive evidence is provided by the high levels of tungsten in the altered granite within the mineralized area. Although the mean $\delta^{18}O$ for the ore fluids (+3.85‰) may be taken as the initial source value, it cannot be distinguished from isotopically lighter fluid which has mixed with heavier fluid from the greisen or primary magmatic fluid. Similarly, at 235°—95°C the $\delta^{18}O$ of the fluids in equilibrium with the greisen is below that normally accepted for magmatic water (Table 8), but at 350°C it is just within the range 7.5—9.0‰ given by Taylor.[18] Without a knowledge of the D/H and water/rock ratios, however, it cannot be demonstrated that the fluids are unequivocally magmatic. Even so, the oxygen isotope data clearly indicate an interaction of isotopically light non-magmatic water with the granite during greisenization similar to the ore fluids. Shown schematically, the various isotopic models are as follows:

Model 1: Non-magmatic fluids   Ore fluid

Model 2: Mixed non-magmatic fluids   Ore fluid

Model 3: Mixed non-magmatic/ magmatic fluids   Ore fluid

Model 4: Combination of models 2 and 3; mixing of magmatic and non-magmatic components prior to greisenization

Either model 2 or model 4, if correct, would considerably strengthen the case for isotopically light ore fluids and would be consistent with the theoretical release of silica from the granite during greisenization and its subsequent deposition in the

veins.[4] The latter model has the additional advantage that it offers an explanation for the origin of the tungsten without postulating an external non-magmatic source. Whether one can still retain the term 'non-magmatic ore fluid' for systems with a minor magmatic component is a matter for debate.

Table 7　Tungsten analyses for Skiddaw granite and Grainsgill greisen (mineral separates)

Locality	Sample number	Rock type	Mineral	Tungsten, ppm
Sinen Gill	CCR-22	Granite	Biotite	2
	CCR-23			2
Caldew River	CCR-50	Granite	Biotite	3
	CCR-51			3
	CCR-53			3
	CCR-55			4
Grainsgill	CCR-46	Greisenized granite	Chlorite	5
	CCR-47			5
	CCR-48			4
	CCR-49			8
	CCR-46		Muscovite	20
	CCR-47			20
	CCR-48			30
	CCR-49			20
	LD 73—60	Greisen	Muscovite	35

Metasomatic alteration alone does not account for the relatively high salinity of the ore fluids. Experimental work has shown that under favourable conditions aqueous fluids of a high NaCl content may separate from a crystallizing magma.[24] Such fluids would be characterized by magmatic $\delta^{18}O$ values[18] and a Na/K ratio of approximately 1.33.[25] Since the corresponding values for this study are quite different, it is unlikely that the NaCl content of the ore fluids was derived solely by this mechanism. Slightly higher Na/K ratios (5—6) can be obtained by equilibration with an albite — K-feldspar assemblage at 300°C, but the overall salinity is very much lower. The observed salinity of the ore fluids is best considered, therefore, as an inherent feature of the fluids prior to their interaction with the granite. With regard to the early deposition of tungsten, the evidence for specific controls is less conclusive. Precipitation of wolframite and scheelite would depend in part on the form in which the metal was carried in solution. From the inclusion data it is evident that the

Table 8　Calculated $\delta^{18}O$ of fluid in equilibrium with greisenized granite Grainsgill outcrop (per mil)

Temperature, °C	Mean $\delta^{18}O$ muscovite	Calculated $\delta^{18}O$ fluid*
265†	+ 9.49	+ 5.20
235‡	+ 9.49	+ 4.20
295§	+ 9.49	+ 6.00

*Calculated from the following equation (from O'Neil and Taylor):[35]

$$10^3 \ln\alpha = -3.89 + 2.38 \ (10^6 \ T^{-2})$$

† Mean muscovite—chlorite temperature, excluding CCR-47.
‡ Mean homogenization temperature (uncorrected).
§ Mean homogenization temperature (corrected for pressure).

physico-chemical state of the ore fluids changed with time, but it does not follow that this was primarily responsible for the mineral zonation in the veins. Rapid changes in CO_2 content (pH control via $HCO_3^- - CO_3^{--}$ equilibria), a fall in temperature, or mixing of fluids of different compositions could each theoretically initiate deposition. Alternatively, the mineral paragenesis could be related to fundamental variations in the level of tungsten in solution and therefore independent of the above. Until, however, the transport of tungsten in a H_2O-CO_2-NaCl fluid at elevated temperatures and pressures is better understood, those factors most likely to cause deposition will prove difficult to define. On the further question of identifying the source of the metal, the oxygen data offer no unique answer. The evidence would appear to support either a magmatic or non-magmatic origin, since massive dilution by isotopically light fluids would tend to conceal a discrete magmatic component. Because sufficient tungsten must be kept in solution for deposition after mixing, the concept of a small magmatic component indirectly substantiates the case for the transport of tungsten in a non-magmatic saline fluid from a source area beyond the Skiddaw granite if required. The role of moderately saline hot fluids, enriched in tungsten and periodically charged with CO_2 under high pressure, during the deposition of the Carrock Fell tungsten deposits is in excellent agreement with the conditions described by Naumov and Ivanova[17] for the quartz—wolframite deposits at Belukha, Bukuka and Dzhida in the U.S.S.R.

As demonstrated by the K—Ar systematics, the final cooling of the Skiddaw granite, the greisenization and tungsten mineralization all occurred within a relatively short period of time, indistinguishable within the limits of analytical error. The observed unreliability of chlorite as a precise geochronometer casts doubt on the illite—chlorite ages reported by Ineson and Mitchell,[26] who proposed an episodic model for the tungsten mineralization over the interval 197—282 m.y.

The apparent crosscutting nature of the quartz veins with respect to the Grainsgill greisen does not conflict with the hypothesis of coeval greisenization—mineralization. This is because fluids rising from lower levels in the granite would tend to select the most open channelways available; hence, deposition would appear to post-date the adjacent greisenized wallrocks. The short interval between the final cooling of the granite and onset of alteration—mineralization suggests the persistence of a high thermal flux, capable of sustaining a natural convective system within and around the intrusive rock. This would provide the ideal conditions for intensive groundwater—rock interaction, and would obviate the need to invoke externally heated fluids.

The restricted location of the mineralized area on the northern flank of the granite was probably determined by the proximity of an active groundwater circulation system. At the time of mineralization, the intrusive rock would have been surrounded to the east, west and south by a broad mantle of relatively impervious Skiddaw slates, recently dewatered by the end-Silurian deformation, whereas to the north lay a thick

sequence of volcanic rocks. Compared to the slates, the highly fractured volcanic rocks, including the equally massive gabbroic rocks of the Carrock Fell complex, would possess a greater aquifer potential. It is thought that the non-magmatic fluids involved in the greisenization—mineralization were modified 'meteoric waters' drawn in from the more permeable volcanic formations to the north. In the context of this paper, meteoric water is defined according to Sheppard, Nielsen and Taylor,[27] and carries with it the full implications of isotopic and chemical exchange with regard to connate water. The gross chemical composition of the fluids (e.g. salinity) suggests they had already undergone substantial modification prior to their interaction with the granite. Various processes exist for generating high saline intraformational fluids from originally dilute fluids (fresh or sea water) (see de Sitter,[28] White,[29] Helgeson,[30] Chilingarian and Rieke,[31] Berry[32] and Edmunds[33]).

Proposed model of ore genesis

From the present data, a tentative working model can be established for the genesis of the tungsten deposits. It is proposed that during the cooling of the Skiddaw granite non-magmatic moderately saline fluids were drawn into the northern part of the intrusive rock by convective flow from the adjacent volcanic country rocks. Under the ambient $P-T$ conditions metasomatic alteration of the granite occurred with greisenization in the Grainsgill area passing outwards into chloritization further south. Because the fluids were also enriched in tungsten, a diffuse geochemical halo was created in the altered granite as a result of preferential tungsten concentration in the metasomatic micas. Having left the greisenized granite, the fluids, now enriched in silica by the breakdown of primary igneous silicates, mixed with further quantities of unreacted non-magmatic fluid. In the Carrock Fell area mixing took place along a series of open channelways provided by a system of north—south faults traversing the granite—slate—gabbro contacts. Within these channelways, conditions were favourable for the deposition of quartz together with smaller amounts of wolframite and scheelite. As the convective system waned, the fluids became slightly cooler and only quartz was deposited. The model has many features in common with the water—rock interaction model proposed by Sheppard and co-workers[27] for the porphyry copper deposits, but differs in other respects because of its geological setting. First, the mineralization is not associated with fine-grained porphyritic rocks or hydrothermal breccias; secondly, it is not characterized by multiple phases of ore deposition as veins, veinlets and disseminations. These differences are probably related to the depth of burial at the time of mineralization and lower water/rock ratios.

Conclusions

(1) The mineralization and associated metasomatic alteration of the Skiddaw granite were coeval, and occurred soon after the emplacement of the granite; but cannot be resolved within the limits of analytical error (minimum age of intrusion 392 ± 4 m.y.; mean age of mineralization— alteration 385 ± 4 m.y.).

(2) The mineralizing fluids were moderately saline NaCl solutions, periodically charged with CO_2 and enriched in tungsten. Isotopically they were depleted in ^{18}O relative to magmatic fluids ($\delta^{18}O < 5.0‰$), and considered therefore to have contained a major non-magmatic component.
(3) Areas of the granite affected by pervasive greisenization or chloritization also indicate equilibration with similar fluids under the same $P-T$ conditions, suggesting a close genetic affinity (greisenization: 240—95°C; fluid composition $\delta^{18}O + 4$ to $\delta^{18}O + 6‰$. Mineralization: 265—95°C; 800 bars pressure; fluid composition $\delta^{18}O + 3$ to $\delta^{18}O + 5‰$).
(4) The alteration—mineralization model most consistent with the data is analogous to that proposed for the 'porphyry coppers', and envisages the interaction of isotopically different fluids with the hot granite. The presence of a magmatic component is less conclusive than for the porphyries and it is only inferred to explain the source of the tungsten.

Significance of model for future exploration

The close spatial relationship between mineralization and greisenization suggests that the primary geochemical halo for tungsten in the altered granite may be used as a guide to mineralized ground. Within this zone the probability of economic vein formation is greatest. South of the Grainsgill greisen, the gradual decrease in mineralization as predicted by the model agrees well with the observed splitting and dying out of the main veins beyond the crest of Coombe Height. North of Grainsgill, the equivalent alteration in the Carrock Fell gabbros is less well developed and does not offer the same potential. Since the subsurface western limit of greisenization is unknown and the mineralization is greatest along the northern margin of the granite, the ground immediately west of the Carrock mine must be considered promising and virtually untested. Similarly, there is a strong possibility of a continuation of ore below the lowest worked levels. One reason, though speculative, for continuation of the active development of the Harding vein in the gabbros may be the presence of greisenized granite at depth, as suggested by the outer limit of thermal metamorphism. Another consideration is the potential use of fluid inclusion studies to test the affinity of apparently barren quartz veins outcropping north and west of Grainsgill Beck to the tungsten-bearing quartz veins.

References

1. Downie C. and Soper N. J. Age of the Eycott Volcanic Group and its conformable relationship to the Skiddaw Slates in the English Lake District. *Geol. Mag.,* **109**, 1972, 259–68.
2. Ward J. C. The geology of the northern part of the English Lake District. *Mem. geol. Surv. Gt Br.,* 1876, 132 p.
3. Harker A. Carrock Fell: a study in the variation of igneous rock masses. *Q.J. geol. Soc. Lond.,* **50**, 1894, 311–37; **51**, 1895, 125–48.
4. Hitchen C. S. The Skiddaw granite and its residual products. *Q.J. geol. Soc. Lond.,* **90**, 1934, 158–200.
5. Eastwood T. *et al.* Geology of the country around Cockermouth and Caldbeck. *Mem. geol. Surv. Gt Br.,* 1968, 298 p.
6. Finlayson A. M. The ore-bearing pegmatites of Carrock Fell, and the genetic significance of tungsten ores. *Geol. Mag.,* **7**, 1910, 19–28.
7. Ewart A. Hydrothermal alteration in the Carrock Fell area, Cumberland, England. *Geol. Mag.,* **99**, 1962, 1–8.
8. Hall A. Greisenisation in the granite of Cligga Head, Cornwall. *Proc. Geol. Ass.,* **82**, 1971, 209–30.
9. North A. A. Geochemical field methods for the determination of tungsten and molybdenum in soils. *Analyst,* **81**, 1956, 660–68.
10. Haas J. L. Jr. The effect of salinity on the maximum thermal gradient of a hydrothermal system at hydrostatic pressure. *Econ. Geol.,* **66**, 1971, 940–6.
11. Vukalovich M. P. and Altunin V. V. *Thermo-physical properties of carbon dioxide* (London: Collet's, 1968), 463 p.
12. Kennedy G. C. Pressure–volume–temperature relations in CO_2 at elevated temperatures and pressures. *Am. J. Sci.,* **252**, 1954, 225–41.
13. Lemmlein C. G. and Klevtsov P. V. Relations among the principal thermodynamic parameters in a part of the system $H_2O–NaCl$. *Geokhimiya,* 1961, 133–42; *Geochemistry,* 1961, 148–58.
14. Takenouchi S. and Kennedy G. C. The binary system $H_2O–CO_2$ at high temperatures and pressures. *Am. J. Sci.,* **262**, 1964, 1055–74.
15. Takenouchi S. and Kennedy G. C. The solubility of carbon dioxide in NaCl solutions at high temperatures and pressures. *Am. J. Sci.,* **263**, 1965, 445–54.
16. Fyfe W. S. Stability of Al_2SiO_5 polymorphs. *Chem. Geol.,* **2**, 1967, 67–76.
17. Naumov V. B. and Ivanova G. F. The pressure and temperature conditions for formation of wolframite deposits. *Geokhimiya,* 1971, 627–41; *Geochem. intn.,* **8**, 1971, 381–94.
18. Taylor H. P. Jr. The oxygen isotope geochemistry of igneous rocks. *Contr. Mineral. Petrol.,* **19**, 1968, 1–71.
19. Brown P. E. Miller J. A. and Soper N. J. Age of the principal intrusions of the Lake District. *Proc. Yorks. geol. Soc.,* **34**, 1964, 331–42.
20. Dalrymple G. B. and Lanphere M. A. *Potassium–argon dating* (San Francisco: Freeman, 1969), 258 p.
21. Kulp J. L. and Engels J. Discordances in K–Ar and Rb–Sr isotopic ages. In *Radioactive dating* (Vienna: IAEA, 1963), 219–38.
22. Evernden J. F. and Kistler R. W. Chronology of emplacement of Mesozoic batholithic complexes in California and Western Nevada. *Prof. Pap. U.S. geol. Surv.* 623, 1970, 42 p.
23. Ivanova G. F. Conditions of concentration of tungsten during greisenization. *Geokhimiya,* 1969, 22–32; *Geochem. intn.,* **6**, 1969, 12–21.
24. Kilinc I. A. and Burnham C. W. Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kilobars. *Econ. Geol.,* **67**, 1972, 231–5.
25. Holland H. D. Granites, solutions, and base metal deposits. *Econ. Geol.,* **67**, 1972, 281–301.
26. Ineson P. R. and Mitchell J. G. K–Ar isotopic age determinations from some Lake District mineral localities. *Geol. Mag.,* **111**, 1974, 521–37.
27. Sheppard S. M. F. Nielsen R. L. and Taylor H. P. Jr. Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits. *Econ. Geol.,* **64**, 1969, 755–77.
28. Sitter L. U. de. Diagenesis of oil-field brines. *Bull. Am. Ass. Petrol. Geol.,* **31**, 1947, 2030–40.
29. White D. E. Saline waters of sedimentary rocks. In *Fluids in subsurface environment – a symposium. Mem. Am. Ass. Petrol. Geol.* **4**, 1965, 342–66.
30. Helgeson H. C. Geologic and thermodynamic characteristics of the Salton Sea geothermal system. *Am. J. Sci.,* **266**, 1968, 129–66.
31. Chilingarian G. V. and Rieke H. H. Some chemical alterations of subsurface waters during diagenesis. *Chem. Geol.,* **4**, 1969, 235–52.
32. Berry F. A. F. Relative factors influencing membrane filtration effects in geologic environments. *Chem. Geol.,* **4**, 1969, 295–301.
33. Edmunds W. M. Geochemistry of brines in the Coal Measures of northeast England. *Trans. Instn Min. Metall. (Sect. B: Appl. earth Sci.),* **84**, 1975, B39–52.
34. O'Neil J. R. *et al.* Stable isotope and chemical relations during mineralization in the Bodie mining district, Mono County, California. *Econ. Geol.,* **68**, 1973, 765–84.
35. O'Neil J. R. and Taylor H. P. Jr. Oxygen isotope equilibrium between muscovite and water. *J. geophys. Res.,* **74**, 1969, 6012–22.
36. Wenner D. B. and Taylor H. P. Jr. Temperatures of serpentinization of ultramafic rocks based on O^{18}/O^{16} fractionation between coexisting serpentine and magnetite. *Contr. Mineral. Petrol.,* **32**, 1971, 165–85.