

The evolution of saline and thermal groundwaters in the Carnmenellis granite

W. M. EDMUNDS

British Geological Survey, Hydrogeology Unit, Wallingford, Oxon OX10 8BB

J. N. ANDREWS

School of Chemistry, University of Bath, Bath BA2 7AY

W. G. BURGESS AND R. L. F. KAY

British Geological Survey, Hydrogeology Unit, Wallingford, Oxon

AND

D. J. LEE

Atomic Energy Establishment, Winfrith, Dorset.

ABSTRACT. The Carnmenellis granite and its aureole contain the only recorded thermal groundwaters (up to 52°C) in British granites. They occur as springs in tin mines at depths between 200 and 700 m and most are saline (maximum mineralization 19 310 mg l⁻¹). Mining activity has disturbed the groundwater circulation pattern developed over a geological time-scale and levels of bomb-produced tritium (> 4 TU) indicate that a significant component (up to 65%) of the most saline waters are of recent origin. All components of all the mine waters are of meteoric origin. Radiogenic ⁴He contents, ⁴⁰Ar/³⁶Ar ratios, and uranium series geochemistry suggest that the thermal component has a likely residence time of at least 5 × 10⁴ years and probably of order 10⁶ years.

The thermal waters have molar Na⁺/Cl⁻ ratios considerably less than 1 but they are enriched relative to sea water in all major cations except Mg. The groundwater is also particularly enriched in Li with contents ranging up to 125 mg l⁻¹. The groundwater salinity, which may reach a maximum of 30 000 mg l⁻¹, is shown to result from weathering reactions of biotite (probably through a chloritization step) and plagioclase feldspar, to kaolinite. On volumetric considerations, fluid inclusions cannot contribute significantly to the groundwater salinity, and stable isotope ratios rule out any contribution from sea water.

Groundwater silica contents and molar Na⁺/K⁺ ratios suggest that the likely equilibration temperature is 54°C, which would imply a depth of circulation of about 1.2 km.

THE Carnmenellis granite in Cornwall and its aureole contain the only recorded thermal ground-

waters (up to 52°C) in British granites. Their origin has been the subject of debate since the metalliferous mines in the region were first developed. Recently, the groundwaters have been reinvestigated as part of the geothermal exploration of the UK (Burgess *et al.*, 1982). The granite is also of special significance as the site of the first European Hot Dry Rock experiment (Batchelor and Pearson, 1979) which involves extracting heat from rocks at depth by circulating water through a fracture system created artificially between two boreholes. An understanding of the natural groundwater flow in the granite is important for two reasons. First, rapid downflow of near-surface water would cause cooling. Secondly, isothermal zones are produced at depth along the vertical axes of groundwater circulation cells and temperature predictions based on heat-flow determinations above upward flowing groundwater would be overestimates of the true value. Such overestimates were made, for example, during exploration at Marysville, USA (ERDA, 1977).

The aim of the present study was to use geochemical evidence to determine the following parameters of deep groundwater circulation in the granite: (i) the temperature of chemical equilibration at depth, (ii) the depth of groundwater circulation, (iii) the residence time of water in the granite, (iv) the source of the salinity, (v) the circulation path

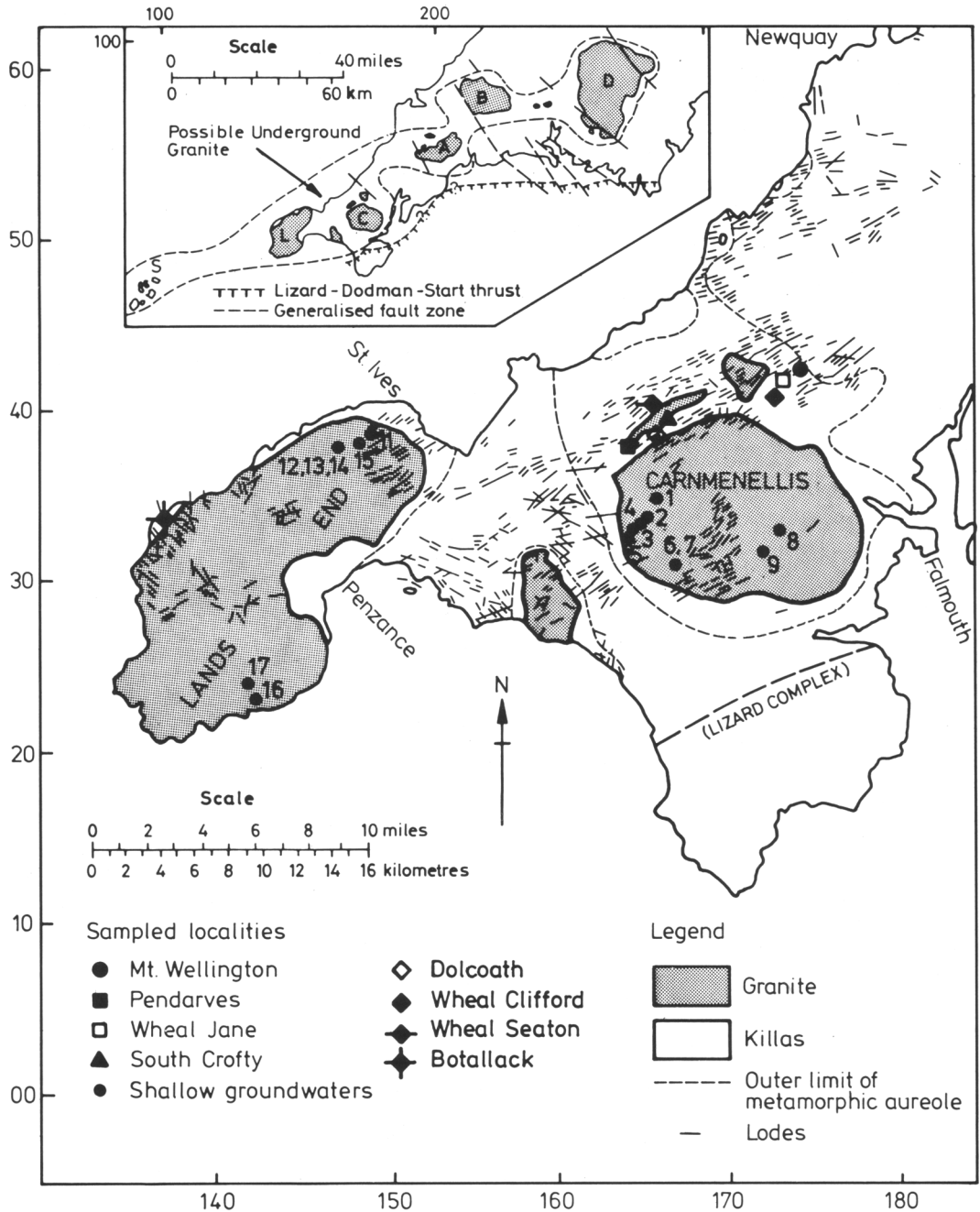


FIG. 1. The geological setting of the Carnmenellis granite in relation to the outcrops of the Cornubian batholith (see inset: S, Scilly Isles; L, Land's End; C, Carnmenellis; A, St Austell; B, Bodmin; D, Dartmoor), after Edmunds *et al.* (1969), showing the location of thermal and non-thermal groundwaters sampled. Shallow groundwater sample 10 is located in the St Austell granite.

of the water, and (vi) the extent of any mixing between influx of recent meteoric water and stored groundwater in the granite.

GEOLOGICAL AND GEOTHERMAL SETTING

The Carnmenellis granite (fig. 1) was intruded into Devonian argillaceous sediments towards the end of the Variscan orogeny, as part of the Cornubian batholith, which has been dated as *c.* 290 Ma (Edmonds *et al.*, 1969; Jackson *et al.*, 1982). The granite is predominantly a micaceous adamellitic granite with quartz, plagioclase (usually oligoclase), orthoclase (often perthitic), biotite, and/or muscovite (Exley and Stone, 1964). It is enriched in boron, lithium, fluorine, and chlorine and commonly carries accessory tourmaline, apatite, and zircon. Boron and fluorine metasomatism has resulted locally in tourmalinization and greisenization. Kaolinization, which is locally extensive, may be of hydrothermal (Sheppard, 1977) or lower temperature origin (Alderton and Rankin, 1983). The granite produced a low grade thermal aureole with cordierite and andalusite. There is strong hydrothermal mineralization with oxides and sulphides predominantly of Sn, Cu, Pb, and Zn. The principal lodes strike between ENE-WSW and E-W in the mineralized belt to the north of Carnmenellis (fig. 1). The main period of hydrothermal activity was also of Variscan age (Jackson *et al.*, 1982).

The Cornubian batholith as a whole is situated in an area of heat flow substantially higher than the average (60 mWm^{-2}) for the UK. The Carnmenellis granite has an average heat flow of about 120 mWm^{-2} (Wheildon *et al.*, 1977) and a value of 129 mWm^{-2} has been calculated (Tammemagi and Wheildon, 1974) for the South Crofty mine, situated on the northern edge of the Carnmenellis granite. The high heat-flow region is now known to extend throughout the Cornish peninsula (Wheildon *et al.*, 1980). Heat production from radioelements (U, Th, K) in the granite is consistently high at about $4.5 \mu\text{Wm}^{-3}$ (Wheildon *et al.*, 1980). Although it has often been suggested that groundwater circulation was partly responsible for the heat-flow anomaly, the recent work implies that convective heat transfer is not significant. The higher thermal conductivity of the granite in comparison with its surrounding metapelite results in the thermal gradients in the granite generally being lower than gradients across the metapelite. The average thermal gradient in the Carnmenellis granite, from several boreholes drilled across its outcrop, is $29.8^\circ\text{C km}^{-1}$ whilst in the mineralized granite, at South Crofty, it is 38°C km^{-1} (Wheildon, pers. comm.). The thermal

gradient in the metapelites is rather more variable ($20\text{--}50^\circ\text{C km}^{-1}$), but in general the lower thermal conductivities in the aureole result in steeper gradients in the immediate vicinity of the granite. The local thermal gradient at Wheal Jane is 45°C km^{-1} .

CHEMICAL ANALYSIS OF GROUNDWATERS

During the present study (1977-8) field determinations were made for temperature, pH, bicarbonate (strictly, total alkalinity as HCO_3^- equivalent), and Eh. Chemical analyses were carried out on samples ($0.45 \mu\text{m}$ filtered in the field) by automated colorimetry and atomic absorption spectrometry using methods described by Cook and Miles (1980). Boron determinations were by inductively coupled plasma optical emission spectrometry. Samples were also analysed for oxygen, hydrogen, carbon, and uranium isotopes, tritium, radium, radon, and inert gases. Shallow groundwater data are listed in Table I and data from mines in Tables IIa and IIb. All but one of the analyses (sample 10) are in ionic balance within 5%. Historical chemical data quoted by Miller (1865), Phillips (1873), Collins (1912), Alderton and Sheppard (1977), and Beer *et al.* (1978) are also used in the discussion.

SAMPLING IN RELATION TO THERMAL WATER OCCURRENCE

Since the development of tin mining in Cornwall there have been records of thermal water encountered in several mines associated with the Carnmenellis granite and its aureole (fig. 1). For the present study all active flows of thermal water in the active mines at South Crofty and Pendarves (both within the granite) and at Wheal Jane and Mount Wellington (both in the aureole) were sampled. The thermal waters are usually saline and their total mineralization ranges up to $19\,310 \text{ mg l}^{-1}$ ($\text{Cl}^- 11\,890 \text{ mg l}^{-1}$) at the deepest level in South Crofty. The relationship between depth, salinity, and temperature is illustrated in fig. 2, relative to the range of thermal gradients in the granite and the country rocks. The hottest water in any mine level is usually also the most saline. The waters in the mines within the metapelite, where the thermal gradient is higher, are usually warmer than those in the granite at the same level. The relationship between discharge temperature, depth, and salinity strongly suggests that the warmest waters have circulated to greater depths than those at which they were sampled.

A total quantity of over $76\,000 \text{ m}^3\text{day}^{-1}$ of groundwater is pumped from these active tin mines.

TABLE I. Site details and results of chemical, radiochemical, and isotopic analyses for shallow groundwaters. Code for sample type: a, pumped sample; b, depth sample; c, tank sample; d, spring; e, stream.

Sample Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Nat. Oxid Ref. (all SK)	669 362	662 350	660 348	658 345	650 344	687 314	687 314	741 338	732 327	995 566	484 398	475 394	475 394	475 394	483 391	419 244	418 252
Sample type	a	a	c	c	d	a	a	a	a	a	a	d	c	d	e	b	b
Depth m	30	32	36	-	0	18	36	6	41	23	57	0	-	0	0	31	32
Temperature °C	10.8	12.4	5.9	12.4	11.5	10.1	10.7	-	-	5.5	-	11.5	-	11.5	8.8	11.0	11.2
pH	4.92	-	5.22	5.64	5.67	4.71	4.79	-	-	5.50	5.33	5.02	-	5.98	6.27	5.26	6.36
DH	-	-	-	-	-	-	+370	-	-	-	-	-	-	-	-	-	-
Na mg l ⁻¹	14	-	27	17	16	18	16	16	12	12	32	23	-	24	19	37	21
K "	2.8	-	10.5	5.0	3.7	9.0	1.5	1.5	4.0	1.5	11.4	1.1	-	8.6	1.7	11.3	24.8
Li "	<0.01	-	<0.01	<0.01	0.01	<0.01	<0.01	-	<0.01	<0.01	<0.01	<0.01	-	<0.01	<0.01	<0.01	<0.01
Ca "	7	-	12	22	11	11	7	13	13	4	35	2	-	12	11	45	28
Mg "	2.7	-	9.1	3.9	4.4	5.4	7.2	2.4	2.4	1.7	9.0	3.1	-	4.3	4.5	15	6.9
Si "	<0.06	-	<0.06	<0.06	<0.06	0.18	0.23	-	0.23	0.06	0.18	0.06	-	0.06	<0.06	0.33	0.38
HCO ₃ "	4	-	11	28	6	2	33.0	-	9	21	17	4	-	21	7	8	82
NO ₃ "	2.07	-	70.0	34.0	29.6	46.0	3.0	-	26.0	2.2	88.9	1.2	-	23.7	22.7	15.3	13.0
SO ₄ "	15	-	23	28	20	21	16	-	17	10	35	14	-	19	16	37	41
Cl "	25	-	47	28	28	36	25	-	21	17	63	41	-	43	36	73	38
F "	<0.1	-	0.36	<0.1	0.16	0.90	0.35	-	0.11	0.40	0.11	0.14	-	<0.01	0.10	0.16	<0.1
SiO ₂ "	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe "	0.280	-	0.410	0.130	0.008	0.052	0.054	-	0.014	0.480	0.026	0.014	-	0.022	0.024	0.025	0.126
Pb "	0.031	-	0.105	0.021	0.024	0.045	0.043	-	0.008	0.045	0.195	0.020	-	0.003	0.009	0.047	0.002
Cd "	0.004	-	0.046	0.040	0.006	0.001	0.013	-	0.027	0.052	0.042	0.002	-	0.003	0.001	0.004	0.005
Ni "	0.0020	-	0.0055	0.0020	0.0030	0.0025	0.0015	-	0.0015	0.0012	0.0035	0.0025	-	0.0030	0.0015	0.0055	0.0050
Total mineralisation	92	-	210	172	119	149	109	-	105	70	291	90	-	157	118	380	255
ionic balance %	-4.9	-	-5.6	-3.1	-2.7	-5.0	+0.9	-	-1.3	-9.3	-0.5	-4.7	-	-2.1	-1.3	-0.6	+0.4
⁶³ Ni per ml SCM	-	-	-	-28	-	-	-	-	-	-33	-	-	-	-	-	-	-
⁶¹ SiO per ml SCM	-	-	-	-5.6	-	-	-	-	-	-6.3	-	-	-	-	-	-	-
⁴ He cm ³ /cm ³ H ₂ O x 10 ⁸	3.2	5.3	-	4.9	6.1	-	5.3	4.6	-	4.4	3.8	5.3	-	-	-	-	-
⁴⁰ Ar/ ³⁶ Ar	-	-	-	-	-	-	295.641.5	-	-	-	296.721.5	-	-	-	-	-	-
U μg kg ⁻¹	0.80±0.05	-	0.90±0.04	0.34±0.03	0.68±0.07	1.85±0.03	1.37±0.03	4.76±0.23	1.18±0.06	1.96±0.11	1.41±0.07	-	0.46±0.01	-	0.30±0.01	1.51±0.06	1.82±0.07
²³⁴ Th/ ²³⁸ U	1.52±0.11	-	0.89±0.03	0.99±0.10	1.08±0.07	1.09±0.02	1.04±0.02	0.83±0.03	0.97±0.04	1.07±0.05	1.14±0.06	-	0.99±0.02	-	1.09±0.06	1.01±0.04	0.95±0.08
²²⁶ Ra	1.8	2.5	17.0	0.7	2.6	2.6	3.9	2.0	0.6	0.6	6.7	1.0	1.0	-	5.4	4.1	-
²²² Rn	9940	18600	6730	6730	21110	-	7960	3080	8170	7320	16100	15270	240	12250	-	3710	-
Ne cm ³ /cm ³ H ₂ O x 10 ⁷	2.08	2.04	-	2.02	1.99	-	2.07	2.04	-	2.09	2.05	2.08	-	-	-	-	-
Ar cm ³ /cm ³ H ₂ O x 10 ⁴	3.81	3.79	-	4.11	3.84	-	4.02	3.79	-	4.01	3.89	3.95	-	-	-	-	-
Kr cm ³ /cm ³ H ₂ O x 10 ⁸	8.14	8.25	-	8.84	8.27	-	8.61	7.99	-	8.74	8.26	8.54	-	-	-	-	-
Recharge T(Av) °C	12.3	12.1	-	9.0	11.8	-	9.9	12.6	-	9.6	11.5	10.6	-	-	-	-	-

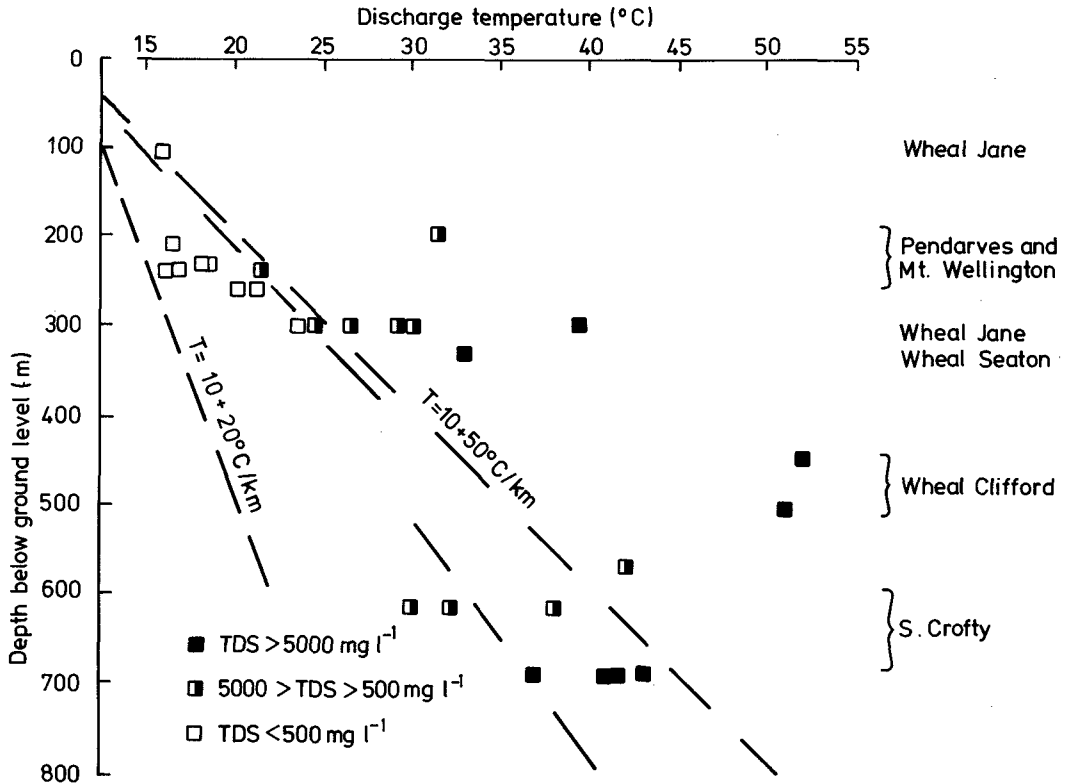


FIG. 2. Relationship between depth, temperature, and salinity for Cornish minewaters. The local thermal gradients at Wheal Jane and South Crofty are also indicated.

The mean temperature of the discharge at the surface is about 15°C, which is 5° above ambient temperature. This produces a pumped thermal yield of 18 MW. Pendarves and Mount Wellington are 'wet' mines in which percolation of groundwater into the workings is common. There are also a few discrete inflows at depths of about 250 m from joints or fractures, and from exploratory drill-holes which intersect these. It was only possible satisfactorily to sample the discrete inflows. Wheal Jane and South Crofty are much drier at the working levels at 300 and 690 m respectively, with water more commonly encountered as discrete inflows related either to joints, cross-cutting faults, or lodes. Samples were taken from each of these structural settings (see Table II), although it has been observed that the major water-transmitting zones result from faulting. Shallow groundwaters were sampled at several localities at outcrop (fig. 1) to assess the granite-water interaction on a short time scale.

DISCUSSION

Origin of the water

All available oxygen and hydrogen isotope analyses of groundwater and surface water from SW England lie close to the world meteoric line (fig. 3) of Craig (1961). Results from the present study confirm earlier observations (Alderton and Sheppard, 1977; Sheppard, 1977) that the thermal groundwater is almost identical to the shallow non-thermal groundwater ($\delta^{18}\text{O} = -5.5 \pm 0.5\text{‰}$) and therefore that the thermal water is of meteoric origin. This demonstrates that the groundwater salinity cannot be marine derived and also suggests that the climatic conditions at recharge for the thermal and shallow groundwaters were similar. Furthermore, the absence of any $\delta^{18}\text{O}$ shift demonstrates that the water has not undergone isotopic exchange with the rock matrix. The recharge temperatures (7–12°C) derived from the contents of dissolved inert gases (Tables I and II) are generally similar for both

TABLE III. Site details and results of chemical, radiochemical, and isotopic analyses from Mount Wellington and Pendarves mines. Sample type code: a, fracture in granite; b, fracture in metapelite; c, cross-cut; d, lode; e, work-face; f, drill-hole; fw, foot-wall; gr, granite; mp, metapelite.

Sample	MOUNT WELLINGTON MINE (SN 748 420)										PENDARVES MINE (SN 647 382)									
	18 6-level Moat West ID f _{mp}	20 7-level Moat Lode B2 d/divide	21 7-level Moat Cross-out c	22 7-level Moat Cross-out d/fw	23 5-level Harride East a	24 5-level Harride East c	25 6-level Harride East d	26 6-level Harride DDI33 f/d	27 6-level Working Face e		23 5-level Harride East a	24 5-level Harride East c	25 6-level Harride East d	26 6-level Harride DDI33 f/d	27 6-level Working Face e					
Sample Type																				
Depth	m	210	240	240	240	260	260	260	260	230	230	260	260	260	260	260				
Porosity	10 ⁻¹	0.8	15	15	0.2					0.1	1.0	0.5	0.1	0.1						
Temperature	°C	16.8	21.6	16.8						18.2	18.6	21.4	20.2	21.4						
pH		5.5	5.0	5.6						6.4	6.5	6.9	7.0	7.0						
Bt	mf	-	-	-	-	-	-	-	-	+30										
Na	mg l ⁻¹	36	37	125	40	40	29	29	29	22	25	29	29	29	29	29				
K	"	3.7	4.3	12	4.5	4.5	3.1	3.1	3.1	2.6	3.6	3.1	2.7	2.7	2.7	2.7				
Li	"	0.63	0.71	3.55	0.77					0.04	0.06	0.06	0.05	0.05	0.05	0.05				
Ca	"	22	26	93	31	31	16	16	16	16	18	18	21.4	21.4	21.4	21.4				
Mg	"	11.8	10.9	11.9	10.4	10.4	6.4	6.4	6.4	6.4	8.6	8.6	6.4	6.4	6.4	6.4				
Sr	"	0.24	0.37	1.43	0.40					0.05	0.06	0.06	0.07	0.07	0.07	0.07				
HCO ₃	"	8	6	9	7	7	51	51	51	43	43	67	75	75	75	75				
NO ₃	"	<0.2	<0.2	11.2	12.4					<0.2	8.7	8.3	<0.2	<0.2	<0.2	<0.2				
SO ₄	"	145	161	275	160	160	53	53	53	51	38	38	60	60	60	60				
Cl	"	72	72	287	80	80	25	25	25	41	32	32	27	27	27	27				
F	"	0.79	0.98	0.29	1.00					0.93	1.10	2.90	2.30	2.30	2.30	2.30				
Br	"	0.3	0.3	0.9	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.9	0.9	0.9	0.9				
B	"	0.05	0.05	0.80	0.17					0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01				
SiO ₂	"	19.3	21.4	19.2	21.4					25.7	29.9	34.2	29.9	29.9	29.9	29.9				
Fe	"	33.25	24.25	43.00	28.85					3.25	5.65	0.62	0.80	0.80	0.80	0.80				
Mn	"	2.37	2.20	2.90	2.10					0.55	0.75	0.30	0.50	0.50	0.50	0.50				
Cu	"	0.003	0.820	0.024	0.021					0.003	0.002	0.002	0.001	0.001	0.001	0.001				
Ni	"	0.150	0.180	0.134	0.160					0.004	0.003	0.007	0.008	0.008	0.008	0.008				
Total mineralisation	"	462	376	885	387					207	227	230	262	262	262	262				
Ionic balance	%	-4.3	-1.1	+1.3	+2.1					-3.8	+0.8	-4.1	-1.3	-1.3	-1.3	-1.3				
δ ² H	per ml SHM	-	-36	-35	-	-	-38	-38	-38	-	-	-38	-	-	-	-				
δ ¹⁸ O	"	-	-5.6	-5.4	-	-	-5.5	-5.5	-5.5	-	-	-5.2	-	-	-	-				
1°C	% modern	-	-	71.643	-	-	-	-	-	-	-	-	-	-	-	-				
δ ¹³ C	per ml FEB	-	-	-19.5	-	-	-	-	-	-	-	-	-	-	-	-				
³ H	TU	27	30	-	-	-	39	39	39	46	46	24	36	36	36	36				
³ He	cm ³ /cm ³ H ₂ O x 10 ⁸	-	328	1360	-	-	7.6	7.6	7.6	-	-	56.8	-	-	38.2	38.2				
⁴⁰ K/ ³⁶ Ar		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
U	kg kg ⁻¹	0.5350.04	2.9040.08	1.4730.03	-	-	0.1450.02	0.1450.02	0.1450.02	-	-	0.2550.03	-	-	0.4350.01	0.4350.01				
²³⁴ m/238U	pCi kg ⁻¹	2.0450.19	1.2650.06	1.9040.08	-	-	2.0650.39	2.0650.39	2.0650.39	-	-	2.7950.50	-	-	1.9650.16	1.9650.16				
²²⁶ Ra	pCi kg ⁻¹	20	7	14	-	-	9	9	9	-	-	13	-	-	195	195				
²²² Rn	pCi kg ⁻¹	4600	1700	2500	-	-	13500	13500	13500	-	-	4300	-	-	126000	126000				
Ne	cm ³ /cm ³ H ₂ O x 10 ⁷	2.00	2.07	2.10	-	-	2.10	2.10	2.10	-	-	2.08	-	-	2.10	2.10				
Ar	cm ³ /cm ³ H ₂ O x 10 ⁴	4.01	3.96	4.26	-	-	4.15	4.15	4.15	-	-	3.97	-	-	4.19	4.19				
Kr	cm ³ /cm ³ H ₂ O x 10 ⁸	8.41	8.37	8.78	-	-	8.74	8.74	8.74	-	-	8.27	-	-	8.89	8.89				
Recharge T(Ar)	°C	9.7	10.2	7.4	-	-	8.4	8.4	8.4	-	-	10.1	-	-	8.0	8.0				
Recharge T(Kr)	°C	11.0	11.2	9.3	-	-	9.5	9.5	9.5	-	-	11.7	-	-	8.9	8.9				

TABLE IIB. Site details and results of chemical, radiochemical, and isotopic analyses for samples from Wheel Jane and South Crofty mines. Sample type code as Table IIA.

Sample	WHEEL JANE MINE (SN 775 426)					SOUTH CROFTY MINE (SN 670 398)				
	28 9-level Working face dye	29 9-level 940	30 9-level 943	31 9-level 944	33 9-level Clemmow's c	35 380-level No. 4 figr	36 380-level No. 4 figr	37 380-level Robinson's a	38 380-level 48 Hrc Dry c	39 380-level 48 Hrc Dry c
Sample type										
Depth	300	300	300	300	300	690	690	690	690	690
Flowrate	4.0	1.0	3.0	3.0	10	3.0	3.0	3.5	3.5	3.5
Temperature	26.8	26.4	29.9	29.5	39.5	37.0	36.8	43.0	41.5	41.5
pH	4.90	5.00	5.80	6.42	6.40	6.80	6.00	6.30	7.21	6.50
EH	+216	-	+148	-	-	+188	-	-	-	-
Na	104	131	950	900	64	465	-	1875	4640	4300
K	13.0	12.0	50.0	48.0	8.6	22.0	-	54.0	135	180
Ca	2.90	3.55	27.0	35.0	1.50	13.0	-	54.0	120	125
Cl	135	110	615	575	53	365	-	1840	2325	2470
Mg	17.9	12.6	41.0	36.1	6.8	36.0	-	139	72.8	73.0
Sr	2.40	1.80	11.2	9.70	0.86	5.40	-	14.3	41.2	40.0
HCO ₃	9	5	50	12	54	117	121	57	64	68
NO ₃	0.8	15	15	8.0	10	-	-	<0.2	-	<0.2
SO ₄	880	540	141	151	140	81	-	102	173	145
Cl ₂	210	330	3000	2540	114	1500	-	7100	11890	11500
F	5.30	4.30	2.70	2.60	3.30	2.00	-	4.50	2.80	2.70
Br	0.7	1.0	10.0	-	0.5	5.0	4.3	12.0	23.0	43.0
B	0.45	0.82	2.5	3.0	0.18	1.5	-	1.3	2.6	11
SiO ₂	29.9	92.0	19.3	18.6	47.1	25.7	-	23.5	25.7	34.2
Fe	245	184	67.7	79.0	14.1	2.22	-	22.6	13.0	4.75
Mn	5.45	3.27	7.65	9.00	1.80	1.45	-	3.72	5.00	4.50
Cu	0.039	1.70	0.066	0.006	0.008	0.003	-	0.005	0.014	0.022
Ni	0.350	0.024	0.025	0.020	0.023	0.006	-	0.019	0.154	0.190
Total mineralisation	1660	1434	4996	4420	511	2642	-	5509	11423	19002
Ionic balance %	44.3	+5.0	-2.2	44.3	+5.5	-2.2	-	-2.4	-0.7	-2.5
⁶³ Zn	-	-	-	-31	-	-33	-	-33	-35	-28
⁶⁷ Zn	-	-	-	-5.7	-	-5.4	-	-5.6	-5.5	-5.2
¹³ C	-	-	-	-	-	-	-	42.950.6	42.451.5	42.451.5
¹³ C	-	-	-	-	-	-	-	-	-18.4	-17.4
³ H	33	-	6.5	6.2	26	7.4	-	13	12	7.4
⁴⁰ K/ ⁴¹ K	848	-	5440	-	-	3520	-	15500	9080	21100
⁴⁰ K/ ⁴¹ K	-	-	-	-	-	-	-	-	-	311.951.5
U	0.1150.03	-	-	-	-	-	-	0.3340.04	0.11+0.003	0.2550.0004
²³⁴ Th/ ²³⁸ U	1.5940.26	-	-	-	-	-	-	1.6150.26	1.7740.31	1.6740.17
²²⁶ Ra	83	-	-	-	-	579	-	416	790	677
²²² Rn	470	-	-	-	-	19800	-	17500	5683	12700
Ne	cm ³ /cm ³ H ₂ O x 10 ⁷	2.07	1.83	-	-	1.48	-	1.55	1.33	0.84
Ar	cm ³ /cm ³ H ₂ O x 10 ⁴	3.86	3.89	-	-	3.13	-	2.41	2.19	2.19
Kr	cm ³ /cm ³ H ₂ O x 10 ⁸	8.34	8.49	-	-	7.17	-	6.97	5.39	5.13
Recharge T(°C)	°C	11.6	11.1	-	-	22.5	-	21.5	39.5	48
Recharge T(K)	°C	11.3	10.6	-	-	18	-	19	32	35

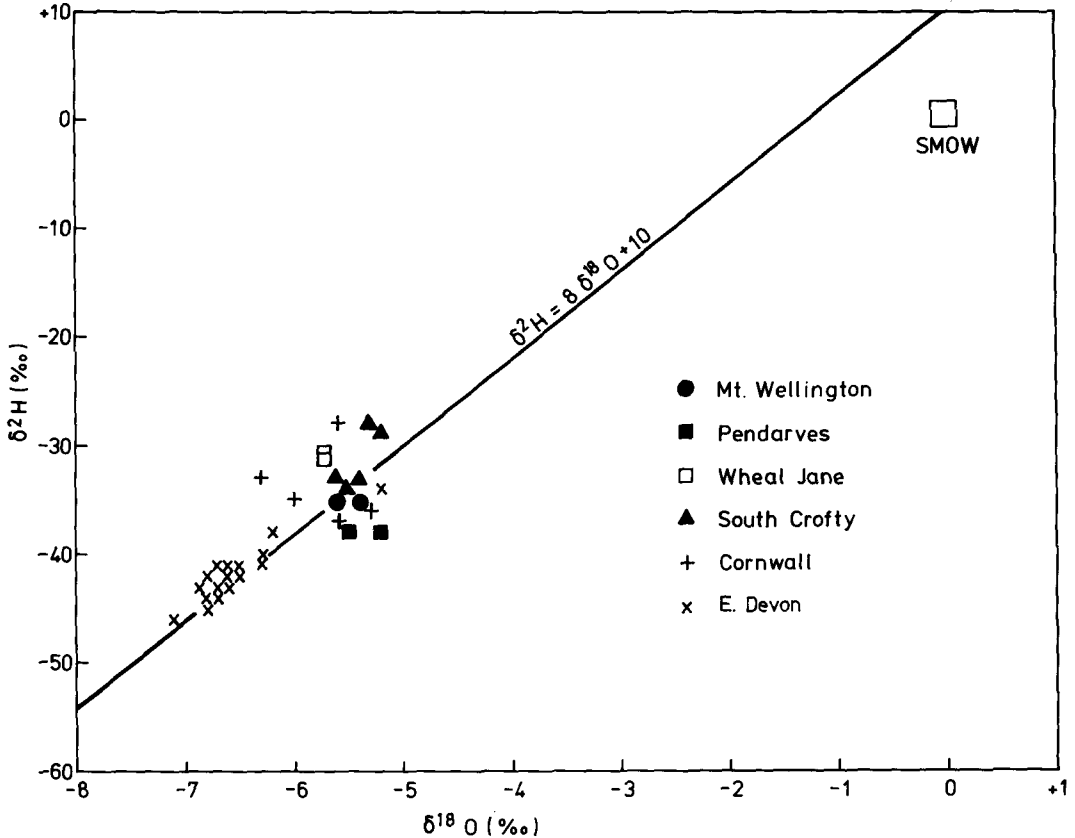


FIG. 3. Plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ for Cornish minewaters as well as shallow groundwaters from Cornwall (this study; Alderton and Sheppard, 1977) and East Devon (Walton, 1982).

deep and shallow waters. This reinforces the view that climatic conditions similar to those of the present day were operative when the deep waters were recharged. The anomalously high recharge temperatures derived from inert gas contents for some South Crofty samples (Table II) were caused by gas loss to the mine air before sampling.

Mixing of recent and old groundwater

The hydraulic sink created by mining activity has disturbed the circulation pattern established over a geological time-scale. Consequently, mixing between recent and old groundwaters is likely to have occurred. This is confirmed by the presence in all the mine waters of significant amounts of tritium, ^3H , ranging from 4.7 to 46 TU* (fig. 4). The more saline minewaters all have ^3H -contents of about 5 TU and this suggested that underground

production of ^3H might be taking place. The high Li and radioelement contents of the granite favour the reaction $^6\text{Li}(n, \alpha) ^3\text{H}$ but it has been shown (Andrews and Kay, 1982) that significant ^3H production by this reaction is unlikely because of the high abundance of the neutron-absorbing element, B, in the granite.

The thermonuclear-weapon ^3H content of UK groundwaters increased after 1954 to about 2000 TU by 1964, and subsequently declined to about 40 TU by 1974 following the cessation of weapon tests in the atmosphere. The maximum ^3H input to groundwaters during this period is unlikely to have a present-day value greater than 80 TU because of radioactive decay of ^3H (Foster and Smith-Carington, 1980). The present-day lower limit for ^3H in groundwater derived from 1954-78 rainfall is approximately 20 TU (fig. 4).

The low-salinity non-thermal waters from Pendarves and Mount Wellington mines have ^3H contents between 23 and 40 TU and must therefore

* TU = 1 tritium unit = one ^3H per 10^{18} H atoms.

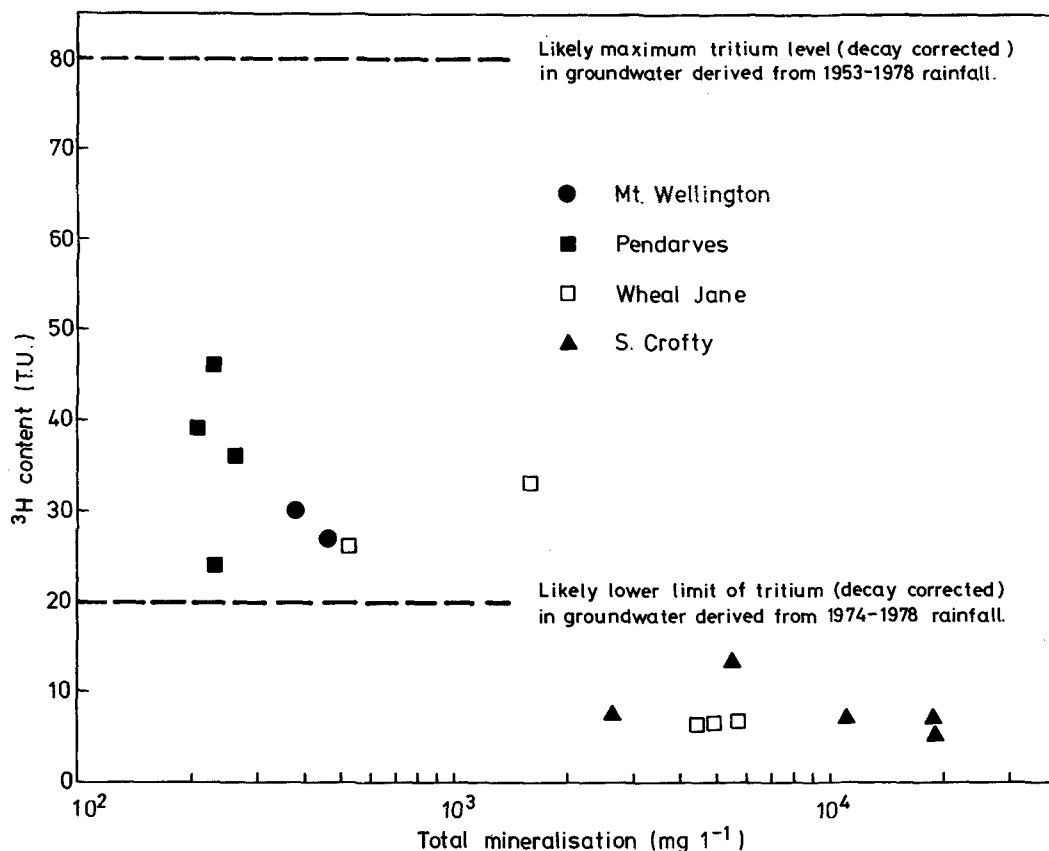


FIG. 4. Plot of tritium, ^3H , against total mineralization for the minewaters.

contain a major proportion of very recent recharge. The thermal waters from South Crofty and Wheal Jane mines, with salinities between 2500 and 19 300 mg l^{-1} , have ^3H contents between 4.7 and 13 TU. These values are too low (< 20 TU) to be the result of decay of ^3H in recently recharged groundwater. They must therefore be due to mixing of a recently recharged component and an older groundwater with only a very low naturally produced ^3H content and with a very high salinity. The proportion of the recent component in the mixtures lies between 6 and 65% depending upon which limiting value of tritium in the recent component is chosen. Thus, the saline component of the mixture may have a salinity up to about 30 000 mg l^{-1} .

Age of the saline component

All samples are probably mixtures of at least two components which makes estimation of ground-

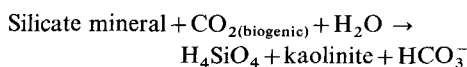
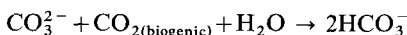
water ages difficult. ^{14}C data, particularly, are very difficult to interpret in such circumstances. A model of groundwater age may be built up using the combined evidence of the excess ^4He content, the excess radiogenic argon, the carbon isotope ratios, and the uranium geochemistry.

The helium, (^4He) contents of the shallow groundwaters are all consistent with air equilibration in the temperature range 9–12 °C (as shown by the other inert gases in Table I). This reflects an insignificant radiogenic helium contribution. All the deeper groundwaters contain excess ^4He (Table II), the amount increasing roughly in proportion to temperature and salinity. Assuming that there is no significant crustal diffusion of helium and if all the ^4He generated dissolves in the fracture fluids, the residence time of the fluid can be calculated from the helium production rate and the radioelement content of the host rock, if the rock density and porosity are known (Andrews and Lee, 1979). Using the radioelement data of Tammemagi and

Wheildon (1974) and assuming a maximum porosity of 1%, then the ^4He age of the most saline water in South Crofty is 400 000 years. If, for example, this source were a mixture with 50% recent groundwater, then the age of the ancient component would be 800 000 years.

Argon isotope ratios were measured on one thermal and two shallow waters. Argon which is dissolved by atmospheric equilibration at recharge has the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of atmospheric argon (295.3:1). Micas and feldspars generally retain much of the radiogenic ^{40}Ar produced by ^{40}K decay within them. As the groundwater migrates in the fracture system some of this stored ^{40}Ar may diffuse into the water and cause an increase in the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the dissolved argon. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of two shallow groundwaters (Table I) are indistinguishable from that of atmospheric argon. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for the South Crofty thermal source, however, is 311.9 ± 1.5 and this corresponds to the addition of $0.28 \times 10^{-4} \text{ cm}^3$ of radiogenic ^{40}Ar to the $5 \times 10^{-4} \text{ cm}^3$ of atmospheric Ar dissolved in each cm^3 of water at a recharge temperature of 10°C . Although this could be interpreted in terms of time dependent diffusive loss (Burgess *et al.*, 1982), it is more likely in the present case that radiogenic ^{40}Ar is being released during alteration reactions. The K-content of the biotite plus orthoclase is about 9% (Al-Turki and Stone, 1978), and the additional ^{40}Ar release would correspond to alteration of 0.2% of the biotite + orthoclase or to alteration of 0.6% of the biotite if the orthoclase is resistant.

Radiocarbon and stable carbon isotope ratio measurements were carried out on samples from three of the thermal springs (Table II). Since ^3H was present, there may also have been some thermonuclear ^{14}C . The ^{14}C content of modern carbon increased as a result of thermonuclear weapon testing and reached a maximum by 1964 of 189% of the pre-1950 value in the UK (Baxter *et al.*, 1969). The observed ^{14}C contents of the thermal waters in Pendarves (71.6% modern) and South Crofty (42.4 and 42.9% modern) could readily be explained by such a ^{14}C input since their ^3H contents show that a substantial proportion of post-1954 recharge is present. The bicarbonate $\delta^{13}\text{C}$ values were in the range -17.4 to -19.5‰ which implies a component of biogenic CO_2 . Bicarbonate could be derived from either of the reactions



Soil zone CO_2 is likely to have $\delta^{13}\text{C}$ close to -25‰ and is probably the main source of CO_2

input. If the second reaction were operating exclusively then all bicarbonate carbon would derive from the biogenic input and have $\delta^{13}\text{C} \approx -25\text{‰}$. Since the bicarbonate $\delta^{13}\text{C}$ values are well above this level, carbonate dissolution also appears to be a contributing process.

The deeper groundwaters do not have significantly higher HCO_3^- concentrations than shallow sources, so it is concluded that carbonate dissolution is occurring principally at shallow depth. No data are available on the $\delta^{13}\text{C}$ composition of hydrothermal carbonates, but if these are important their isotopic composition should be lighter than about -7‰ . An alternative source would be trace carbonate derived from the soil or phreatic zone, also likely to have a composition close to -7‰ and to approximate to modern ^{14}C . A 1:1 mixture of such a soil carbonate with soil CO_2 would give $\delta^{13}\text{C}_{\text{HCO}_3^-}$ compositions close to those observed and the radiocarbon input would be entirely of recent carbon. This would also suggest that there is little incongruent carbonate solution in the phreatic zone. Therefore whilst the $\delta^{13}\text{C}$ values provide a clue to the source of carbon, the radiocarbon results cannot be used to determine groundwater age.

The uranium series geochemistry and in particular the departure from equilibrium of the $^{234}\text{U}/^{238}\text{U}$ activity ratio may be used as an indicator of age. For the near-surface groundwaters from the Carnmenellis granite the average uranium content is $1.4 \mu\text{g kg}^{-1}$, and the $^{234}\text{U}/^{238}\text{U}$ activity ratio is generally close to the equilibrium value (Table I). With the exception of the sources in Mount Wellington mine, all the minewater samples have ^{238}U contents less than $0.5 \mu\text{g kg}^{-1}$ and all have activity ratios which are significantly enhanced (Table II). The minewater sources are clearly distinguished from the near-surface groundwaters by this change in uranium geochemistry.

Redox potentials in minewaters were greater than +30 mV and the pH varied between 5.5 and 7.2 (Table II). Under these conditions, uranium should be mobile (Langmuir, 1978; Andrews and Kay, 1983). However, the minewaters have much lower uranium contents than the shallow groundwaters so that uranium deposition has undoubtedly occurred during their migration to depth.

Consideration of the *radon contents* of the groundwaters (Table I) and their controls (Andrews *et al.*, 1982) suggests it is improbable that there has been any extensive deposition of uranium on fracture surfaces. Since the ^{222}Rn contents of the groundwaters lie on a single log-normal distribution (Burgess *et al.*, 1982), and do not vary systematically with depth, the U distribution in the granite and its fracture porosity are apparently similar throughout

the profile investigated. There may, however, be some localized U deposition from groundwaters in restricted areas of the fracture system. This is indicated by the Pendarves sample, 25, which has an exceptionally high radon content as well as the highest $^{234}\text{U}/^{238}\text{U}$ activity ratio. Secondary uraninite is known in South Crofty and low-temperature pitchblende is found in veins in the aureole. Other uranium secondary minerals are commonly found but the overall distribution of uranium is presently unknown.

Theoretical models for the evolution of $^{234}\text{U}/^{238}\text{U}$ activity ratios for dissolved U in the Stripa granite have been discussed by Andrews *et al.* (1982). It is probable that the South Crofty waters have similarly evolved through a shallow recoil-dominated zone of limited extent, where their activity ratios reached a value ≥ 2 at a depth around 250 m (fig. 5), and that their present activity ratios are the result of either ageing or mixing with groundwaters with an equilibrium activity ratio. In fresh fractures in the granite, for which the surface uranium content is identical with that of the bulk granite, recoil solution of ^{234}U is not significant for fracture openings of about 1 mm or greater. Groundwater which entered such fractures, even if it did so with an enhanced $^{234}\text{U}/^{238}\text{U}$ ratio, would reach isotopic equilibrium after one million years ($T_{1/2}$ for $^{234}\text{U} = 248\,000$ years). Such fracture-stored water

could mix with younger groundwater from the recoil-dominated zone, and the activity ratio of the mixture would diminish with an increase in the proportion of the ancient (equilibrium) end-member. The U chemistry of the South Crofty source at 689 m, samples 38 and 39, could be derived by mixing about 50% of water from the shallower recoil-dominated zone (at about 250 m) with an ancient end-member stored at depth in the fracture system. Alternatively, if the water with a high $^{234}\text{U}/^{238}\text{U}$ activity ratio (from about 250 m) displaced the deeper fracture fluids, it would require about 65 000 years for its activity ratio to decrease by decay to the present value. The tritium and carbon-14 evidence suggests that the mixing model is more plausible and the saline component is therefore likely to be of the order of 10^6 years old.

The ^{226}Ra contents of the shallow groundwaters range from 0.6 to 17 pCi kg^{-1} and are log-normally distributed with a mode at 1.3 pCi kg^{-1} , while the ^{226}Ra contents of the minewaters are bi-modally distributed (Burgess *et al.*, 1982). The deepest and highest temperature waters have markedly greater ^{226}Ra contents (80–720 pCi kg^{-1}) than the cooler, shallower minewaters (7–20 pCi kg^{-1}). The $^{226}\text{Ra}/^{238}\text{U}$ activity ratio undergoes a marked increase during groundwater evolution. This ratio is usually between one and ten for the shallow groundwaters but values of up to several thousands are common in the minewaters. The increase in this ratio is a consequence of the solution of ^{226}Ra by alpha-recoil becoming more significant in the older groundwaters, and of U deposition. The increase in the $^{226}\text{Ra}/^{238}\text{U}$ ratio and the increase in the absolute ^{226}Ra content of the minewaters are therefore indicators of a groundwater ageing trend. Various factors, including the chemical differences between radium and uranium, the mixing in the Cornish groundwaters of young and old groundwater components in uncertain proportions, and the relatively short half-life of ^{226}Ra (1620 years) combine to ensure that these parameters can only be used qualitatively as indicators of relative groundwater age.

In summary the balance of evidence suggests that the age of the saline component in the thermal groundwaters is of order 10^6 years.

The chemical composition of the minewaters and the origin of groundwater salinity

The chemistry of the groundwaters can be explained with reference to log-log plots of dissolved species vs. chloride (fig. 6a–h). The Na^+/Cl^- plot (fig. 6a) shows that all the saline waters (except Botallack) are significantly (about 30%) depleted in sodium relative to sea water, although dilute

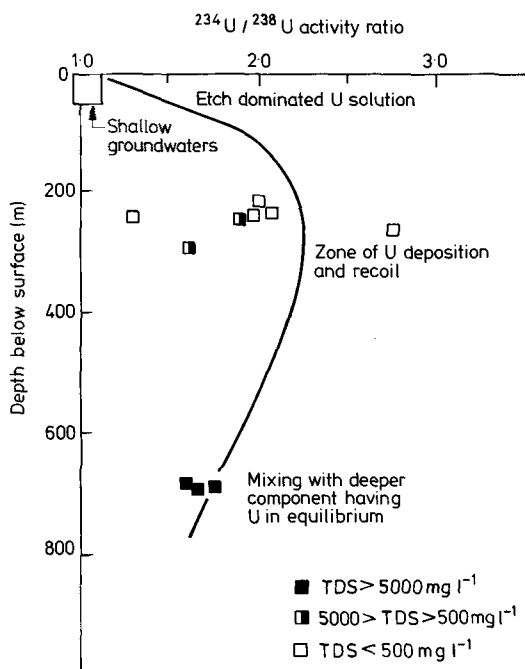


Fig. 5. Trend of $^{234}\text{U}/^{238}\text{U}$ activity ratios with depth.

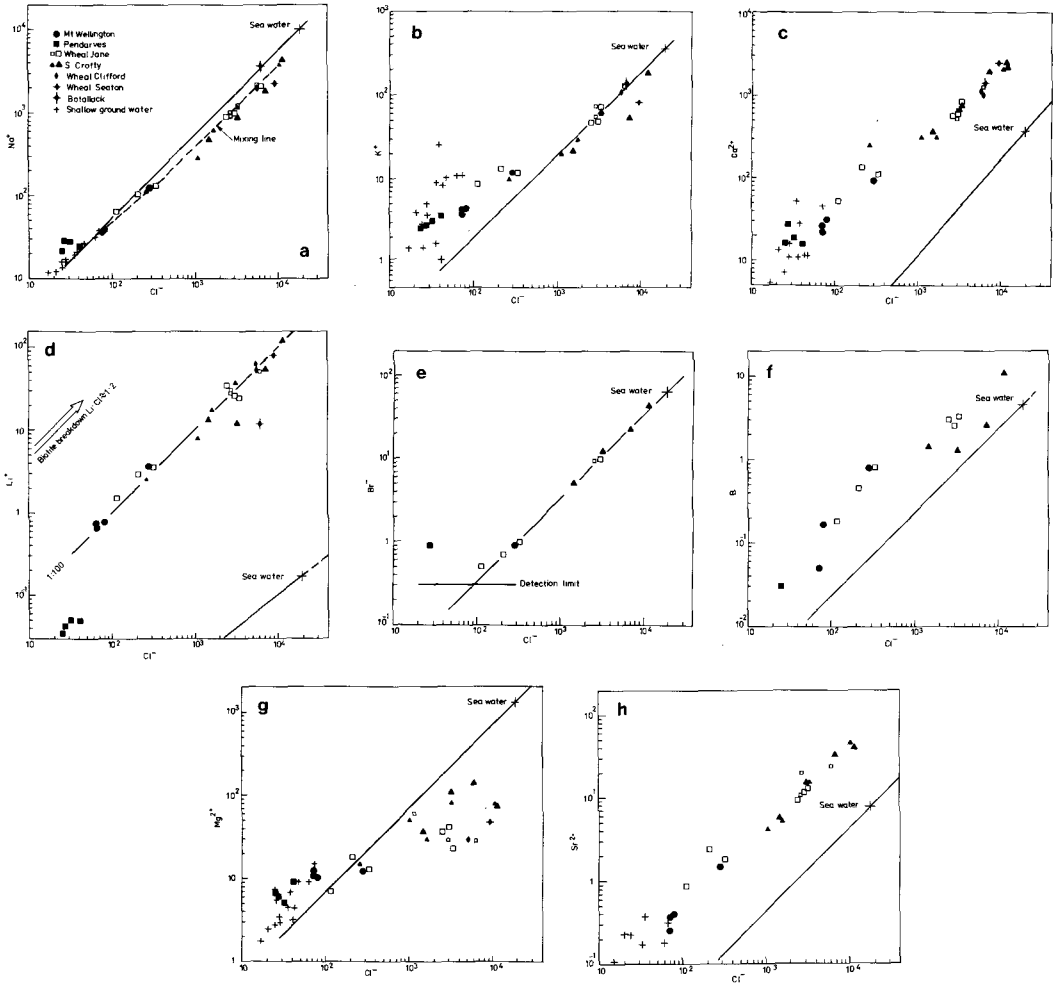


FIG. 6. (a-h) Variation of the dissolved species Na^+ , Ca^{2+} , K^+ , Li^+ , Br^- , B, Mg^{2+} , and Sr^{2+} with chloride content (all mg l^{-1}). The available historical data are included for comparison and are indicated by smaller symbols.

groundwaters retain molar Na^+/Cl^- ratios closer to one indicating a marine aerosol source. The anomalous water from Botallack, a mine near the coast, almost certainly demonstrates a single case of sea-water intrusion. Fig. 6c shows that Ca^{2+} is uniformly enriched in the groundwaters relative to sea water. The K^+/Cl^- ratios (fig. 6b) are lower in the saline waters but the variable content of K^+ in shallow groundwaters is related to high NO_3^- contents and therefore indicates an anthropogenic source. This illustrates the difficulty of obtaining reliable data on inputs to the granite, and in subsequent discussion only those groundwaters with $< 5 \text{ mg l}^{-1} \text{NO}_3^-$ are used.

The most outstanding feature of the chemistry of

the saline waters is their extreme enrichment in Li. This ranges up to 125 mg l^{-1} in the most saline waters, and there is a good linear relationship with respect to Cl^- (fig. 6d). The ratio Li^+/Cl^- is 1:100, except for Pendarves mine water where there is a ratio of 1:650. Lithium and chloride are considered the most important indicators of the extent of water-rock interaction since, unlike other elements which are likely to be affected by secondary mineral formation, they are not subsequently removed from solution. Br^-/Cl^- shows an apparent trend identical to sea water (fig. 6e); this is anomalous. The Br^-/Cl^- ratio in igneous biotites (Fuge, 1974) is similar to the groundwater ratio and this is considered to be the source of bromide in this case.

It has been established that the mine waters are primarily a mixing series between a saline end-member ($20\,000\text{--}30\,000\text{ mg l}^{-1}$) and relatively fresh water, although both are of meteoric origin. In the absence of sea water, proposed, for example, by Frapé and Fritz (1982) as the origin of salinity in groundwaters in crystalline rocks of the Canadian Shield, the source of the salinity must lie in the rocks themselves—either from fluid inclusions or from primary or secondary mineral breakdown. Nordstrom (1983) has recently proposed that fluid inclusions are the origin of groundwater salinity (up to 630 mg l^{-1}) in the Stripa granite in Sweden. These waters compare with those from Carnmenellis in having water $\text{Na}^+/\text{Ca}^{2+}$ depletion relative to sea water, as well as depleted Br^-/Cl^- ratios.

In the Carnmenellis granite a number of different generations of fluid inclusions are abundant in primary and vein quartz, as well as to a lesser extent in other minerals (Sawkins, 1966; Bradshaw and Stoyel, 1968; Rankin *et al.*, 1982; Rankin and Alderton, 1983). Average salinities are between about 10 and 20 wt. % NaCl equivalent ($60\text{--}120\text{ g l}^{-1}\text{ Cl}^-$), on rare occasions ranging up to 40 wt. % NaCl equivalent, although inclusions are also found with very low salinities (Rankin *et al.*, 1982). Al-Turki and Stone (1978) gave the ranges of modal compositions for principal minerals of the main Carnmenellis granite rock type as quartz 31–36%, K-feldspar 28–33%, plagioclase 24%, biotite 3–6%, and muscovite 5–7%. Fluid inclusions are most abundant in quartz and occur in the volumetric range of 0.1–1% and thus at 0.031–0.36% in the modal analysis. The contribution from fluid inclusions to the rock chloride could not generally exceed 170 ppm. This is less than 35% of the average Cl^- content of 507 ppm, for the Cornubian batholith as a whole (Fuge and Power, 1969) which is itself between two and three times the world granite average.

Silica solubility is controlled by chalcedony (fig. 7) which is a metastable product of the silicate mineral breakdown reactions discussed below. Therefore, solution of silica minerals, quartz in particular, is likely to be inhibited. This suggests that fluid inclusions in quartz will be inert under the prevailing groundwater conditions and explains why the high temperature features of fluid inclusions are preserved. This is supported by the cation chemistry of the fluid inclusions (Rankin *et al.*, 1982). The gravimetric Na^+/K^+ ratios range between 2:1 and 13:1 whilst the ratios in groundwater increase regularly to over 30 as salinity increases. The $\text{Na}^+/\text{Ca}^{2+}$ ratios in groundwaters are also considerably enriched (2:1) in calcium relative to the fluid inclusions (generally greater than 10:1). The bulk of the increased contents

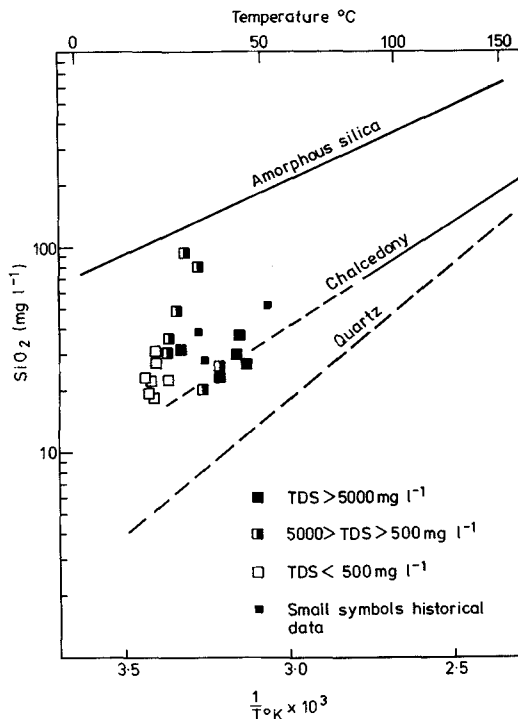


FIG. 7. Silica contents plotted against the reciprocal of temperature, shown in relation to the solubility limits of silica polymorphs (Fournier, 1970).

of dissolved species in the older and saline waters must therefore be due to mineral breakdown. Since the element ratios are so systematic (fig. 6), it also seems that such reactions dominate the chemistry of many of the dilute groundwaters.

All groundwaters fall in the stability field of kaolinite (fig. 8) and kaolinization reactions of biotite and feldspar are probably the most important sources of groundwater salinity. The bulk of chloride not contained in fluid inclusions must be contained in biotite (or possibly muscovite) occupying the interlayer positions usually occupied by hydroxyl (Al Saleh *et al.*, 1977). Using a modal analysis of 5% for the biotite, an unaltered biotite could be expected to contain up to 8500 ppm Cl^- . The granites are also enriched in Li. The Carnmenellis granite and related biotite-adamellites have a mean Li content of 278 (range 40–473 ppm) and contain biotites with reported Li contents in the range 650–6500 ppm (Beer *et al.*, 1978). A reasonable average value for the Carnmenellis biotites is 1800 ppm Li^+ . In contrast, the available evidence shows that Cl^- and Li^+ are depleted in altered granite and in vein minerals.

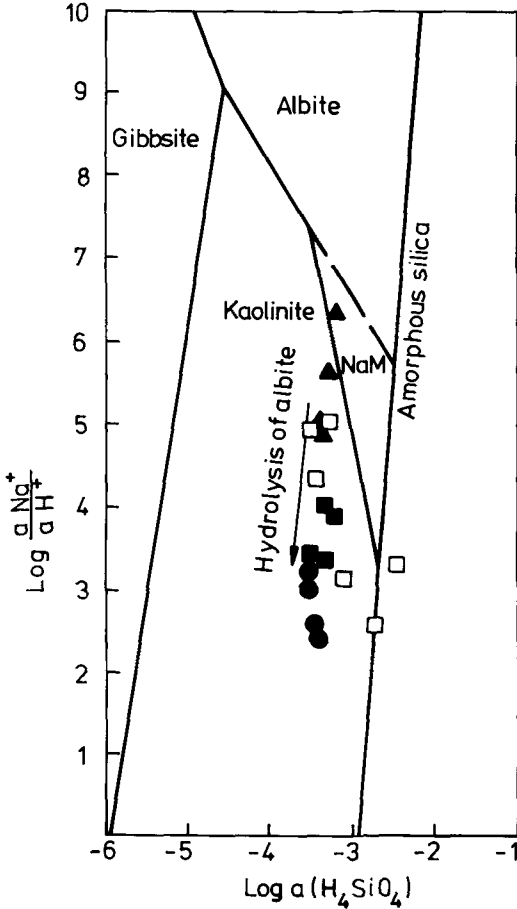
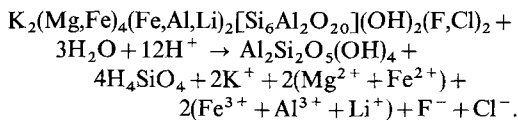


FIG. 8. Relation of samples from the Cornish mines with respect to the mineral stability fields in a plot of $\log a(\text{Na}^+/\text{H}^+)$ against $\log a(\text{H}_4\text{SiO}_4)$. Key is the same as for fig. 6. NaM = sodium montmorillonite.

Both Li^+ and Cl^- can be derived from breakdown of biotite. Li^+ is present in the layers of octahedrally coordinated atoms and most of the Cl^- occupies hydroxyl positions. This reaction can be written for the appropriate case of an iron-rich biotite with significant Li^+ and halogen content:



In reality the Li^+ and Cl^- contents are unlikely to exceed a few atom % per formula unit. The ratio of Li^+/Cl^- in the groundwater (1:100) is much lower than would be expected if it were controlled solely by biotite breakdown (fig. 6d). Using the

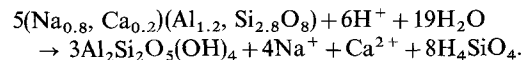
estimates for Li^+ and Cl^- contents of biotite derived above a Li^+/Cl^- ratio as high as 1:5 might be expected. The considerable chloride excess probably indicates that interlayer chloride has exchanged with OH^- without involving structural breakdown of the biotite. The interlayer alteration could easily be as much as twenty times the structural breakdown necessary to account for the observed groundwater chemistry.

Fluoride is only present up to 5 mg l^{-1} in the groundwaters although it would be expected to be released in a manner analogous to Cl^- . The observed aqueous levels are supersaturated with respect to fluorite (Burgess *et al.*, 1982) and it is clear that the Ca^{2+} levels control the maximum fluoride in solution (allowing for complex ion formation). The release of significant amounts of F^- from biotite breakdown should therefore result in fluorite deposition.

Boron (fig. 6f) also increases regularly with salinity and the absolute levels (maximum 11 mg l^{-1}) are between five and ten times those of sea water. The source of boron, like Li^+ , is also likely to be substitution for Al^{3+} in the octahedral layer of biotite, being released primarily during structural breakdown.

Mg correlates very poorly with Cl^- (fig. 6g) and for saline waters is depleted relative to the seawater dilution line. There is also a very low molar $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 0.1:1. This implies that Mg^{2+} is held in the silicates during alteration whereas halides and most other cations are released. The most likely explanation is that kaolinization of biotite proceeds through a chloritization step. The product of such a reaction has a formula approximating to $(\text{Mg, Al, Fe})_{12}(\text{Si, Al})_8\text{O}_{20}(\text{OH})_{16}$. Chlorite is common in Cornish granites and could also form as a thin lamellar alteration but remain difficult to detect.

Ca^{2+} and Na^+ are likely to be largely derived from feldspars. For the oligoclase composition of Carnmenellis plagioclase the hydrolysis reaction to kaolinite may be written:



The molar $\text{Na}^+/\text{Ca}^{2+}$ ratios in the minewaters vary between 1.3 and 4.0. These are lower than that predicted from the stoichiometry of the reaction, suggesting either a degree of preferential dissolution of more anorthitic feldspar or an incongruent process. Orthoclase feldspar is usually stable during kaolinization and its contribution to the solution chemistry is probably minor compared with plagioclase hydrolysis (Exley, 1959; Bristow, 1969). The most probable source of dissolved K^+ is therefore also the biotite reaction, although

removal of K^+ is to be expected during formation of secondary muscovite or other hydro-micas. Strontium shows a regular enrichment with salinity (fig. 6h) up to a maximum of 40 mg l^{-1} . These values are well below celestite saturation, which is the limiting control on solubility under the aquifer conditions (Burgess *et al.*, 1982). The strontium levels are similar in biotite and plagioclase (200–400 ppm) and either or both of these minerals could be the source of dissolved Sr.

Both kaolinization reactions depend upon a continuous supply of H^+ , and the removal of products, for their progress. Dissolved CO_2 , which is often high in recharging waters due to the high pCO_2 levels in the soil zone (Pačes, 1972) and oxidation of sulphide minerals are possible sources of hydrogen ions. The $Cl^- \rightleftharpoons OH^-$ exchange during the biotite breakdown reaction may also be a significant source of H^+ , since the increased electrostatic interactions resulting from higher chloride and/or fluoride in solution would lead to further dissociation of H_2O . This partially self-perpetuating biotite breakdown reaction (assuming SiO_2 precipitates) appears to release many of the solutes into solution and provides the driving force for the kaolinization of feldspar, which further contributes to the salinity.

Levels of transition metals are rather high in certain waters. Very high iron and low pH values are found in Wheal Jane and Mount Wellington mines which indicates that oxidation of sulphide minerals is also occurring. This process leads to enhancement of the other metals to a variable extent but the Fe/metal relationships are not systematic. The processes of trace metal accumulation are most complex in the shallow recent groundwaters and the picture is undoubtedly complicated by precipitation of secondary hydroxides and silica. It should be noted that transition metal contents in the deepest, warmest, and most saline thermal waters are greater than in the shallow groundwaters but are less than the values found in groundwaters from the aureole.

The temperature at depth

The concentrations of dissolved silica and the dissolved alkali element ratios have been used in many geothermal areas to determine water/rock equilibration temperatures at depth (Ellis and Mahon, 1977). In the present case, the existence of mixing rather limits the application of geothermometry, although in other respects the mineralogy and water-rock relationships are favourable. Dissolved silica concentrations are plotted against the reciprocal of sample temperature in fig. 7. The most saline (evolved) groundwaters tend to group around

the chalcedony solubility line rather than quartz and it is likely that chalcedony, which is also a common vein mineral in the granite (Dines, 1956), is the polymorph controlling solubility. If the chalcedony control is accepted, silica geothermometry (Fournier, 1970) gives a maximum temperature of $54^\circ C$ for the most saline groundwater, although this value may be in error due to mixing.

An empirical inverse relationship has been found between the dissolved Na^+/K^+ ratios and temperature (Ellis, 1970; Fournier and Truesdell, 1973) which substantiates trends found in experimental work for feldspar and muscovite dissolution. The relationship between $\log Na^+/K^+$ and sampling temperature is shown in fig. 9, together with the Ellis (1970) empirical line. The observed linear $\log Na^+/K^+$ ratio increasing with rising temperature is considered to represent a mixing relationship between the lower salinity (low Na^+/K^+) and higher salinity (higher Na^+/K^+) groundwaters. The extrapolation of this line to the intercept suggests an equilibrium temperature for the bulk of the saline fluid of $54^\circ C$. The implication from this and the silica geothermometry is that chemical equilibrium was reached at $54^\circ C$ and, for a geothermal gradient of $38^\circ C \text{ km}^{-1}$ this should occur at a depth of 1.1 to 1.2 km.

The scale of water-rock interaction

Some of the saline discharges appear, from historical records, to have been fairly constant for some 100 years, and thus quite considerable volumes of granite are represented by the 'catchment' of any one spring with high salinity. In order to derive the chloride content ($11\,890 \text{ mg l}^{-1}$) of the most saline groundwater at South Crofty it would be necessary to react 23.5 kg of rock (having 507 ppm chloride; Fuge and Power, 1969) for every litre of saline water. If it is assumed that the flow at South Crofty 'Hot Dry' spring has been constant at 3.5 l s^{-1} during this period and that 80% of this is the saline component, then a storage of at least $8.8 \times 10^{-3} \text{ km}^3$ is indicated. Complete structural breakdown of biotite in $6 \times 10^{-3} \text{ km}^3$ of granite, to produce the amount of lithium, together with complete interlayer $Cl^- \rightleftharpoons OH^-$ exchange in 0.1 km^3 of rock, to release chloride, would need to be involved to account for the discharge of dissolved salts from this system in 100 years (Burgess *et al.*, 1982). Since no part of the granite has been completely altered in releasing these species, and only a proportion of the total discharge is represented by this spring, the volume of partially altered granite must be much greater than 0.1 km^3 . If the total volume of the approximately 80 km^2 area of the Carnmenellis outcrop (fig. 1) to a depth

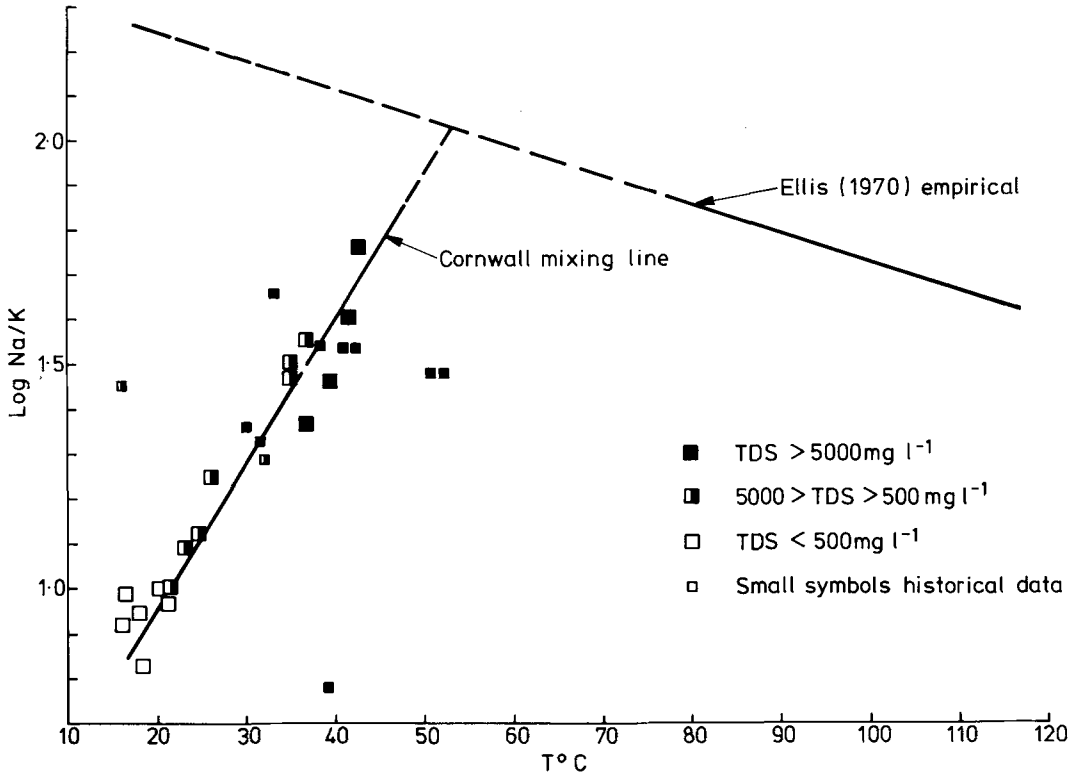


FIG. 9. Trend of log molar Na^+/K^+ against sampling temperature for the minewaters, in relation to the empirical curve of Ellis (1970).

of 1.2 km were involved, and the average fracture porosity does not exceed 1% (Alexander *et al.*, 1981), then the flow of saline water to the Hot Dry spring over the past 100 years would represent about 1% of the total volume of stored fluids.

SUMMARY AND CONCLUSIONS

The Carnmenellis granite contains the only thermal groundwater recorded in granite in the British Isles. The circulation of waters, solutes, and heat is summarized conceptually in fig. 10, where the mixing between recent fresh water and ancient saline water is illustrated. The saline groundwater is of the order of 10^6 years old. It would have circulated on a geological time-scale in response to hydraulic head differentials, especially sea-level changes during Pleistocene glaciation, and any tectonic movement. Present-day natural circulation of the deeper system should also take place at a very slow rate, providing there is hydraulic continuity of fissures. The main circulation observed today, however, has been induced or greatly

accelerated by the mining activity and this has caused the observed mixing between the recent and older systems. On the basis of the equilibration temperatures, the maximum depth of circulation of the system activated by mining operations is likely to be 1.2 km.

The high salinity of the groundwater originates from the alteration of biotite and plagioclase feldspar. The recognition of water-rock reaction as the origin of the salinity has been greatly assisted by the enrichment of volatile constituents in the granite, notably lithium, chloride, and boron. Such reactions may be equally important in the development of groundwater salinity in granites elsewhere. The relative importance of water-rock reactions and other possible origins for salinity needs to be further assessed from studies in other granitic terrains. However, it has been demonstrated that, in the Cornish system, neither sea water nor fluid inclusions is the major source of salinity.

The geochemistry of thermal water has remained constant since the earliest records (1864). This implies a consistent flow regime over the last 100

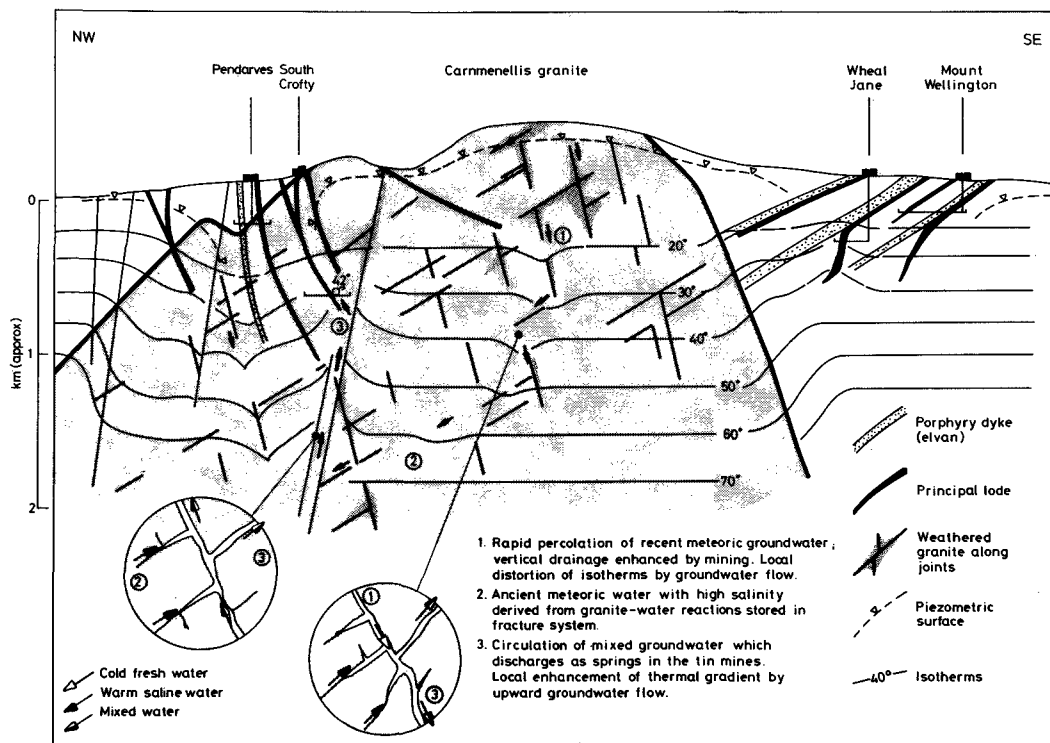


FIG. 10. Conceptual summary of groundwater circulation in the Carnmenellis granite.

years. The chemical model predicts that a change to less saline water inflows to the mines must eventually take place. In addition, it is clear from the mixing model that any water encountered at depths greater than 1 km is likely to have a salinity in the range 20 000–30 000 mg l⁻¹.

Examples are given in this study of mineral-forming reactions (e.g. of fluorite, chlorite, kaolinite, chalcedony) which are a direct response of water-rock reactions in the range 20–55°C. It is also important to recognize that reactions identified in groundwaters aged about 10⁶ years are also taking place at the present day. The data suggest that the current circulation system (albeit modified by mining) is a continuation of that which produced the metalliferous deposits for which the region is well known. This concurs with the view of Durrance *et al.* (1982).

It is clear that natural circulation of groundwater occurs within the granite to considerable depths. This implies that fracture permeability is an important feature of the Carnmenellis granite, especially on its northern flank and this is significant in relation to geothermal development. It is important that further field, experimental, and

theoretical studies be made in relation to artificial exploitation of this and other granites.

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