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THE IONIC COMPOSITION OF SURFACE WATERS IN THE ENGLISH LAKE DISTRICT, RELATED TO BEDROCK GEOLOGY, WITH SOME SINGULAR FACTS AND SPECULATION ON THE EXISTENCE OF MINERAL-RICH GROUNDWATERS

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Introduction

All natural waters are a cocktail of particulate and dissolved substances, including numerous elements that are present in trace amounts, several plant "nutrients" in small to moderate amounts (particularly nitrogen, phosphorus and silicon), and "major ions" or electrolytes (charged solutes) in moderate to relatively large amounts. The major cations are sodium, calcium, magnesium and potassium, plus hydrogen and aluminium which occur in increasingly greater amounts in acid waters, especially at pH below ca. 5.0. Major anions are chloride, sulphate, nitrate and several components representing "alkalinity" - especially bicarbonate and silicates. Although few in number, these ions determine aspects of water quality that are essential for all aquatic organisms. Sodium, potassium and chloride are vital minerals for internal regulation of blood and tissue cells in animals, and tissues of plants. Calcium, magnesium and bicarbonate alkalinity are also vital for the biota, and are the principal components of water "softness" and "hardness". Nitrate is an important plant nutrient, together with phosphate (and silicate for diatoms). Sulphate is a major component of some tissue cells and important in the external environment as a principal anion for maintaining charge balance (electroneutrality), especially in providing a "balance" for hydrogen, calcium and magnesium cations. In this latter role sulphate is important in acidification processes affecting soils and waters, although it is frequently present in larger amounts in hard waters.

Following earlier work by Mackereth (1957) and Gorham (1958), detailed accounts and discussion of numerous factors affecting the ionic composition of surface waters in the English Lake District are given by Sutcliffe et al. (1982), Sutcliffe (1983) and Sutcliffe & Carrick (1983a,b, 1988). The work focussed on waters draining the central hills of the Borrowdale Volcanic series of extruded igneous rocks, especially in the catchments of Windermere and the Duddon valley, although some attention was also given to all of the major lakes. In this article I adopt a broader view, based on a survey of tarns, conducted mainly but not exclusively in the summers of 1983 to 1985, and a survey made in the winter of 1985, in which streams were sampled (during base-flow conditions) on the wide variety of rock-types occurring on the
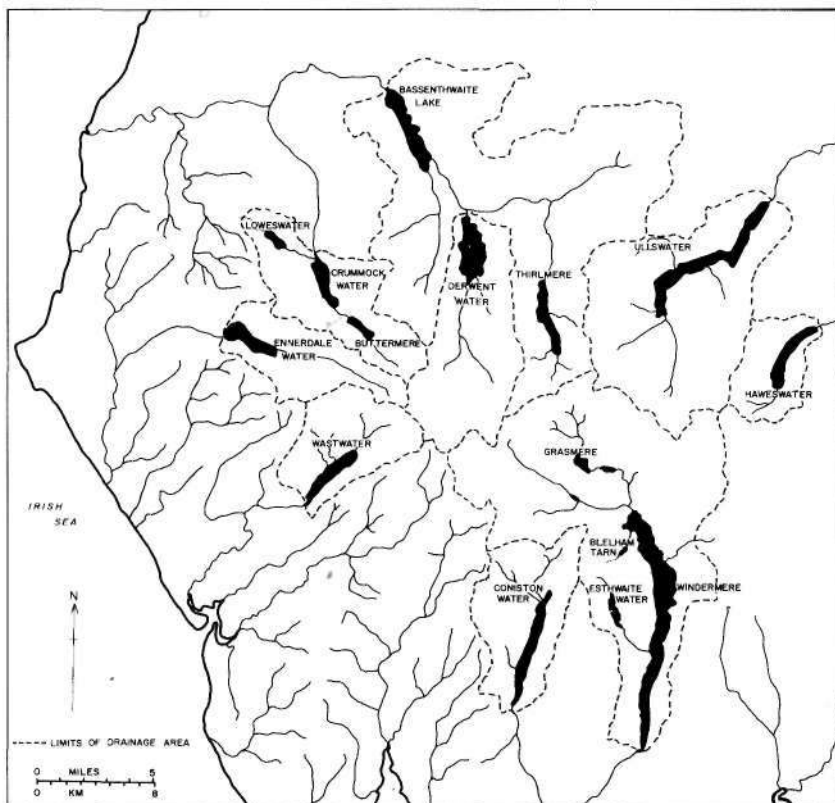
FIG. 1. Major lakes and main drainage areas of the English Lake District (Ramsbottom 1976).

fringes of the Lake District National Park. The survey was done in part to assess the relative contributions from atmospheric deposition, compared with that from catchment rocks and soils, in determining the ionic composition of streamwaters and their subsequent effects on the composition of recipient major lakes in the district. Some well established facts and conclusions are briefly presented here, together with several peculiar anomalies and somewhat speculative explanations for them. Particular emphasis is placed on the concentrations of chloride found in surface waters, because it is believed that this ion is rarely and scarcely present in most bedrocks, having been leached away into oceanic waters during geological time. This chloride is then continually recycled via atmospheric uptake from the sea-surface and deposited back onto land, in relatively large amounts in the case of islands and the coastal

regions of large continents with oceanic climates. As the chloride present on a catchment is thus largely or entirely independent from geological sources within that catchment, except where saline deposits occur, it provides a convenient and indeed essential baseline marker for assessing the likely derivations of other major ions present in surface fresh waters.

The English Lake District and major rock-types

The district lies within the old kingdom and modern county of Cumbria in northwest England, west of the northern Pennines, north of Morecambe Bay and south of the Solway Firth (Fig. 1). This region is one of markedly contrasting relief and rainfall, with deeply dissected glacial dales (valleys) and high fells (mountains and moorland) sprinkled with numerous (ca. 200) small tarns (ponds and pools) and, at lower altitudes (below 300 m) in most of the dales, one or more larger glacial lakes. Rainfall is highest in the central fells around Scafell and the top of Borrowdale, exceeding 150 inches or 450 cm per year, decreasing to below 150 cm on the low-lying fringes of the district (Pearsall & Pennington 1973; Sutcliffe & Carrick 1983a).

The major rock-types in the region are shown in Fig. 2. Extruded lavas of the Borrowdale Volcanics form the western, central and eastern fells of Lakeland, with notable igneous intrusions in Eskdale, Ennerdale and at Shap (O'Brien et al. 1985). Shallow mineral soils are thinly covered by acid peat. The northern fells are formed from slightly older Ordovician Skiddaw Slates, covered in places by very shallow and peaty topsoils. The southern region is mainly low-lying land (below 300 m) on younger Silurian Slates, where soils are predominantly free-draining loams and brown earths, although in places there are poorly-drained peaty gleys covering glacial drift derived from the underlying Slates. Surrounding the higher ground of the Lake District there is a series of well-weathered Carboniferous, Permian and Triassic rocks and associated loamy soils (Moseley 1978; Pennington 1984; Johnson 1985).

Mid-Ordovician in age, the Borrowdale Volcanic Group of rocks (Green Slates and Porphyries) are relatively hard, slow-weathering extrusive lavas comprised of acidic rhyolites and basic calcalkaline andesites. Secondary minerals include calcite (calcium carbonate), epidote and chlorite (silicates), and sericite formed from alkali-feldspars. These impart varying amounts of sodium, potassium, calcium, magnesium, bicarbonate and sulphate ions to surface waters after contact with soils and, especially, the underlying rocks. Nevertheless, as will be shown below, on the higher fells the ionic content of streams and tarns basically resembles that of rainfall, thereby providing a useful baseline for comparison with waters at lower altitudes and on other rock-types in the district.

The Ordovician Skiddaw Slates are the oldest rocks, marine in origin and comprised of mudstones, flags, grits and shales. The younger Silurian Slates

N

Carboniferous
Series

Skiddaw Slates

Sandstones

Borrowdale Volcanics

Igneous Intrusions

Coniston Limestone
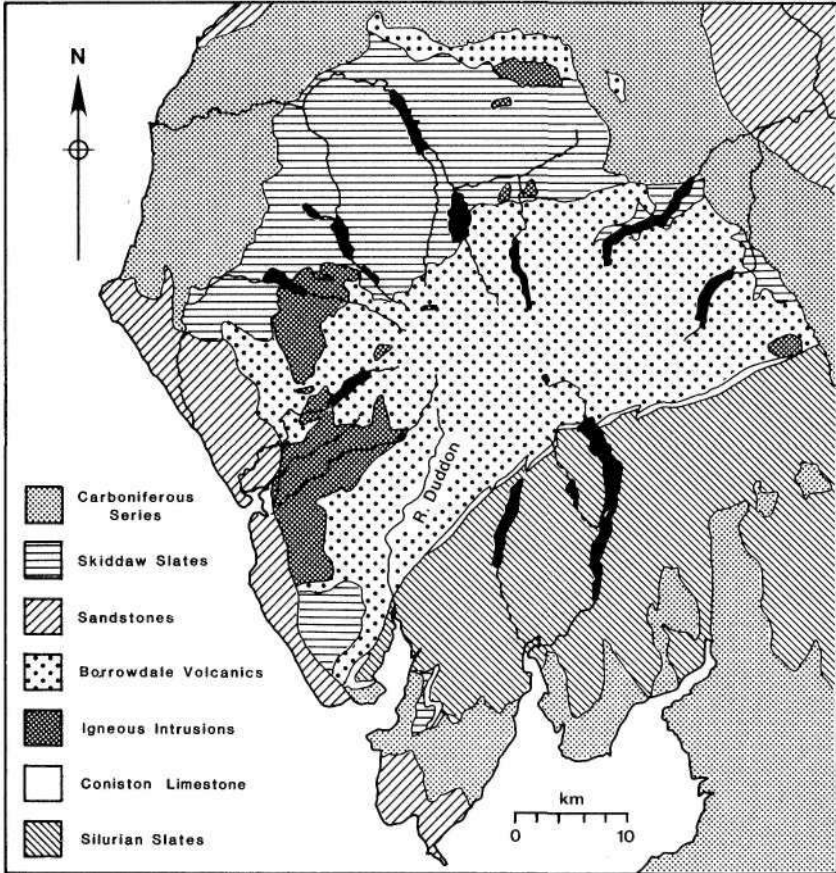
Silurian Slates

R. Duddon

km

0   10

FIG. 2. English Lake District: major rock-types in relation to the larger lakes and the River Duddon in Dunnerdale. The igneous intrusion in the catchment to the east of the Duddon is Eskdale Granite, with Wastwater lying on it and extrusive Borrowdale Volcanics at the inflow end of the basin; to the north the intrusion is Ennerdale Granophyre, with Ennerdale Water lying across it and Skiddaw Slates at the outflow end of the basin (Sutcliffe 1983).

are also marine sedimentary rocks, comprised of flags, grits and shales. Between these and the Borrowdale Volcanics there is a thin band of Coniston Limestone, which noticeably increases the hardness of all surface waters draining to the south of the outcrop, including Windermere and Coniston Water.

Sources of major ions in Cumbrian surface waters

Water falling on the catchments normally enters streams, tarns and lakes by three main routes (e.g. see Tipping 1990, 1996). (1) During periods of high rainfall, surface runoff directly enters watercourses, thereby temporarily diluting the concentrations of some ions in streams and surface waters of tarns and lakes, whilst the concentrations of hydrogen and dissolved aluminium are raised. (2) Water percolates into the soil, consisting of an upper organic horizon and lower mineral horizon, and moves laterally downhill into the nearest stream. (3) Water percolates down through the soil horizons (often only a few centimetres deep on the higher fells) and makes contact with the underlying bedrocks in the unsaturated zone, before finally entering a stream. This last route is an important source of ions leached from the rocks by water that initially is relatively acid and, as is well known from studies in the Lake District and elsewhere (e.g. Bennion et al. 1997), the ionic composition of most waterbodies is directly related to the rock-types on the catchment.

A fourth source - deep groundwater held in rocks, and rising to the surface in some localities, will be discussed at the end of this article.

In Cumbrian fresh waters, all major ions except sulphate (which is rather unpredictable from year to year), exhibit regular and pronounced annual fluctuations. Thus concentrations of calcium, pH and bicarbonate alkalinity are normally maximal in mid-summer and minimal in mid-winter, whereas sodium, potassium, chloride and nitrate are maximal in mid-winter and decline to minima in mid-summer. It is important to take account of these natural fluctuations when considering differences within and between years and the effects of different bedrocks on water composition. Generally speaking, calcium is the dominant cation associated with bicarbonate alkalinity, and the two fluctuate in unison.

Assessing the principal sources of major ions deposited on catchments

Atmospheric deposition on catchments is a primary source of major ions (Table 1). Chloride and sodium predominate, followed by sulphate, calcium, magnesium, nitrate and hydrogen ions. Deposition is acidic. In the 3-year period 1983 to 1985, bulk deposition had an overall mean pH value of 4.9 (13 μ equivalents H+ per litre), compared with a pH of ca. 4.4 (40 μeq H+ per litre) in the mid-1970s.

Rainfall and dry deposits supply (seasonally) variable amounts of some ions that are known or believed to be derived from the sea and continually recycled through the catchment. When this marine or "sea-salt" component is deducted from the combined concentrations for deposition measured at seven sites in Cumbria (Table 1), the resultant values are zero for sodium, chloride and magnesium, 24 microequivalents per litre for calcium, 3 for potassium and 45

Table 1. Mean concentrations of major ions (microequivalents per litre) in deposition on the English Lake District and in tarnwaters on Borrowdale Volcanics (BORVS) during 1983 to 1985. Deposition was measured at seven sites around the Lake District; column 2 gives volume-weighted means for the seven samplers over the 3-year period; columns 3 and 4 show concentrations of ions multiplied by factors of 1.33 (= 25% evapotranspiration) and 1.40 (= ca. 29% evapotranspiration). Negative values for alkalinity (Alk) are equal to positive acidity (H+). Overall means shown for tarns on BORVS were calculated from:- 13 samples from softwater Red Tarn on Helvellyn (Alt 718 m), means for 8-14 samples from each of eleven upland acid tarns (Alt 480-655 m), means for 5-15 samples from each of twelve upland softwater tarns (Alt 436-597 m), and means for 5-12 samples from each of five softwater tarns at medium altitudes (187-316 m).

Variable	Deposition 7 sites	x 1.33	x 1.40	Tarns on BORVS at 436–718m Red Tarn	Acid	Softwater	at 187–316m Softwater
n	7	–	–	(13)	11	12	5
Alt (m)	113	–	–	718	552	510	266
Alk	−13	−17	−18	34	−19	29	33
pH	4.9	4.8	4.8	6.5	4.7	6.3	6.5
Cl⁻	141	188	197	162	178	194	196
NO_3^-	21	28	29	25	16	25	15
SO_4^{2-}	59	78	83	77	83	96	109
Na^+	111	148	155	140	157	164	163
K^+	6	8	8	7	8	11	10
Ca^{2+}	29	39	41	111	47	114	130
Mg^{2+}	27	36	38	53	44	60	50
Na/Cl	0.79	–	–	0.86	0.88	0.85	0.83

for sulphate. Such adjusted mean values provide baselines for estimating the extra amounts in deposition that have been derived from non-marine sources - both local and distant, especially in the case of airborne sulphate and nitrate that are known to travel long distances as components of "acid rain". Similarly, relatively substantial amounts of ammonium ions are also deposited on Cumbria (Sutcliffe et al. 1982; Tipping 1990, 1996), but this has not been shown in Table 1; NH_4^+ is only occasionally found at measurable concentrations in Cumbrian surface waters (usually under ice in the littoral region of shallow tarns).

Thus the major non-marine components of deposition in Cumbria are calcium, hydrogen and ammonium cations, balanced by sulphate and nitrate. About half of the potassium is non-marine in origin, and small amounts of sodium and chloride probably also originate from non-marine sources.

Calcium, alkalinity and pH in surface waters

Concentrations of calcium and alkalinity (Alk) are strongly correlated. In most waters, bicarbonate (HCO3) and carbonate (CO_3^{2+}) ions are principle
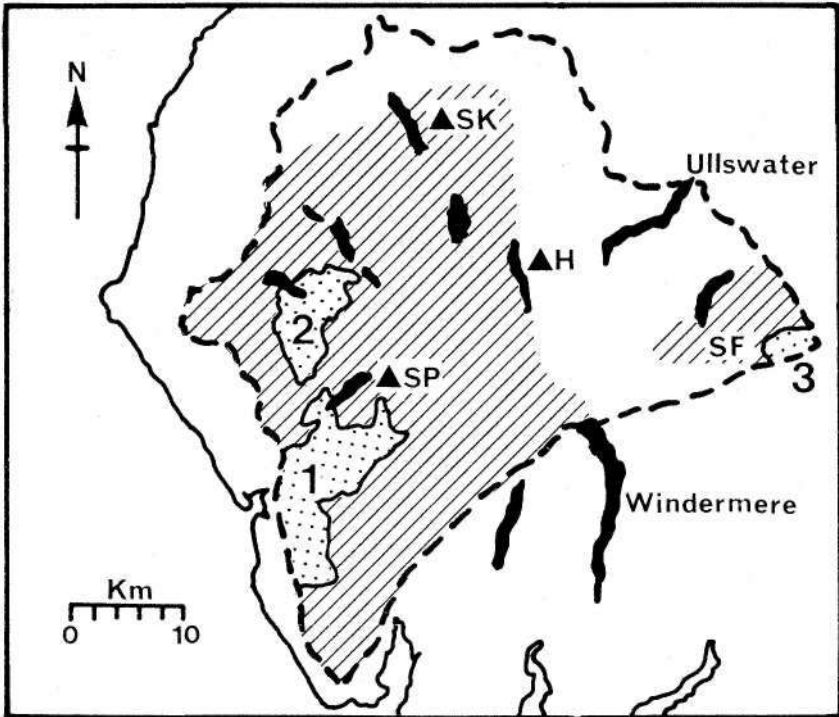
FIG. 3. English Lake District: outline map showing the distribution of acid and very soft waters (hatched areas) on the western Borrowdale Volcanics, Skiddaw Slates and igneous intrusions at 1, Eskdale, 2, Ennerdale and 3, Shap. H = Helvellyn (950 m); SF = Shap Fells; SK = Skiddaw (931 m); SP = Scafell Pike (978 m). The positions of major lakes are shown in black.

components of Alk where this has positive values when determined by Gran titration; negative values indicate the presence of free hydrogen ions or "positive acidity", usually accompanied by increasing amounts of toxic aluminium (Tipping 1989, 1990). For Cumbrian waters a mean concentration of 0 μeq per litre for Alk is equivalent to a value of 5.4 for mean pH (Sutcliffe & Carrick 1988). Maberly (1996) gives a detailed account of the ionic species represented by Alk in Esthwaite Water.

On the Borrowdale Volcanics (BORVS) there is a notable geographical difference in the general distribution of pH, calcium and Alk in surface waters. On the fells east of a line between Ambleside (at the head of Windermere), Thirlmere and the Skiddaw massif, few streams and tarns have negative values for Alk and pH values below 5.4 (Fig. 3). Moreover Alk and calcium are

Table 2. Mean altitudes and concentrations of selected major ions (microequivalents per litre) in streams at altitudes below 200 m on western Borrowdale Volcanics (BORVS), Skiddaw Slates (SKIDS), Ennerdale Granite (ENNG), Eskdale Granite (ESKG), Silurian Slates (SILS) and Carboniferous Limestone (CARB) around Crosby Ravensworth and Lower Lune Valley (east and south-east of the National Park). All streams were sampled at baseflow during winter (January to April) 1985. n is the number of streams, each sampled on 1-4 occasions.

Variable	Western BORVS	ENNG	SKIDS	ESKG	ESKG	SILS	CARB
n	25	8	29	13	7	16	16
Alt (m)	104	133	134	95	29	85	116
Alk	67	75	32	18	125	859	2570
pH	6.5	6.2	6.0	5.8	6.5	7.7	8.0
Cl^-	177	175	241	249	435	387	543
NO_3^-	34	20	27	19	36	112	101
SO_4^{2-}	108	106	112	183	247	109	374
Na^+	165	187	214	239	361	302	386
K^+	7	8	9	14	23	34	53
Ca^{2+}	170	105	114	118	273	1075	2948
Mg^{2+}	66	85	100	88	150	310	455
Na/Cl	0.93	1.07	0.89	0.96	0.83	0.78	0.71

Table 3. Mean concentrations of major ions (microequivalents per litre) in tarnwaters on Skiddaw Slates (Alt 195–610 m), Silurian Slates (Alt 65–320 m), Eskdale Granite (Alt 60–297 m) and Carboniferous-Permian-Triassic series of rocks (CPT; Alt 14–200 m), each sampled on 1–2 occasions during the summer of 1983. Loweswater was sampled (n = 8) in 1984. Chapelhill Tarn (CT; n = 31) and Parkgate Tarn (PT; n = 34) on ESKG were sampled during 1983 to 1985; negative Alk = H^+. Mockerkin Tarn (Mock) was sampled in 1983.

Variable	SKIDS 8 tarns	Lowes	SILS 75 tarns	ESKG 8 tarns	CT	PT	CPT 17 tarns	Mock
Alt (m)	314	121	184	151	152	58	73	115
Alk	170	149	452	59	−27	−42	2996	545
pH	6.1	6.9	7.3	6.1	4.5	4.4	7.7	7.1
Cl^-	225	359	351	267	849	767	476	519
NO_3^-	5	40	4	6	4	18	14	2
SO_4^{2-}	289	166	208	183	272	260	345	289
Na^+	198	271	267	230	668	601	383	370
K^+	19	18	20	18	22	23	66	48
Ca^{2+}	756	307	533	137	154	144	2864	756
Mg^{2+}	143	128	165	93	188	173	640	143
Na/Cl	0.88	0.75	0.76	0.86	0.79	0.78	0.81	0.71

frequently present in relatively high concentrations, with overall means (μeq per litre) of 235 Alk and 322 calcium in 30 streams on the eastern BORVS. On fells to the west of the line, acid streams and tarns that permanently or temporarily (in winter) have pH values below 5.4 (and negative Alk) are more numerous (Fig. 3). Nevertheless adjacent waterbodies may differ considerably, providing an unpredictable mosaic of streams and tarns with none, very small or small amounts of Alk - generally less than 100 μeq Alk per litre at altitudes above 400 m (Sutcliffe & Carrick 1988).

Eskdale Granite (ESKG) and the Ennerdale Granophyre (ENNG) are acidic igneous intrusions. On these rocks, and on the ancient marine Skiddaw Slates (SKIDS), there is a range of acid and low-alkalinity waterbodies (Tables 2 and 3). A few are strongly and permanently acid, especially on ESKG where Chapelhill and Parkgate tarns have particularly low pH values (Table 3), probably derived from iron pyrites in the bedrocks.

Noticeably higher concentrations of calcium, Alk and pH occur on Silurian Slates (SILS) in the southern part of the Lake District, where there are no acid waters. On rocks of the Carboniferous, Permian and Triassic series (CPT), around the fringes of the Lake District, streams and lakes are all rich in calcium and Alk, with pH values above 7.0 (Tables 2 and 3).

Chloride and sodium concentrations in surface waters on BORVS

Mean concentrations of chloride in upland tarns and streams on BORVS are similar to a value (188 μeq per litre) calculated by assuming that 25% evapotranspiration of water occurs after deposition on the catchments (i.e. mean deposition at seven sites Xl.33, column 3 in Table 1). This also applies to the majority of streams on western BORVS at altitudes below 200 m (Table 2), where mean chloride in 25 streams was 177 μeq per litre. Similar results, though with less concordance, were obtained with sodium. If the actual rate of evapotranspiration is less than 25% per annum on the upland catchments lying on BORVS, which is quite likely (Carder 1990), one must assume that some dry deposition, including sea-salts, has occurred unrecorded, i.e. it was not caught by the samplers employed in this study. In fact the dry deposition of sea-salt on exposed coastal areas is sometimes very evident in autumn and winter, causing salt-burn and die-back of vegetation; on these occasions at least, smaller amounts are probably deposited well inland. Occult deposition by mists and clouds on high ground is another extra source of sea-salts (Neal et al. 1988). In general, chloride concentrations are markedly higher in surface waters close (<10 km) to the Irish Sea, and they rise at decreasing altitudes (Sutcliffe & Carrick 1983a,b).

When the original recorded mean values for deposition are multiplied by a factor of 1.40 (column 4, Table 1), good agreement is obtained with 3-year (1983-1985) mean values for chloride and sodium in Levers Water and

Wastwater (see Table 4), whereas mean chloride in Seathwaite Tarn agrees better with column 3 (factor of 1.33) in Table 1. These three waterbodies, all located on western BORVS, appear to be reasonably good indicators of all major ion inputs by atmospheric deposition, with relatively minor inputs of sodium, calcium, magnesium, potassium, sulphate and nitrate from the catchments (plus small amounts of potassium and aluminium silicates derived from the dissolution of feldspars). This is particularly true for Levers Water, a glacial corrie tarn lying in a rocky basin at 411 m above sea-level and used as a small reservoir for drinking water. This tarn is ideal for monitoring the effects of long-term changes in atmospheric deposition; in recent years it has become less acid (Tipping et al. 1998).

Thus major proportions of chloride and sodium in surface waters on western (and eastern) BORVS are due to the cyclical transport of sea-salts between sea, land, and back to the sea (Eriksson 1960), with concentration by evapotranspiration on the catchments. In Cumbria this cyclical transport of sea-salts is markedly seasonal, being most pronounced in the autumn and winter months when westerly gales blow across the Atlantic Ocean and the neighbouring Irish Sea. Chloride and sodium deposited on catchments at this time are slowly washed out, producing a slow exponential fall in streamwater concentrations during spring and summer, followed by a sharp rise during the following autumn. Concentrations in lakes naturally follow the same pattern, and the ratios of Na/Cl also alter seasonally as sodium is released from rocks and soils (Sutcliffe & Carrick 1983b).

Nevertheless, on occasions in some places, the chloride concentrations in streams are higher than would be expected from deposition alone, sometimes markedly so. In Lower Dunnerdale some of the tributaries of the River Duddon have relatively high concentrations of chloride and sodium, both in winter (mean Cl = 310 μeq per litre in 1985) and in summer when concentrations are at their lowest (Sutcliffe & Carrick 1983a,b): in 1984, chloride concentrations ranged from 227 to 249 μeq per litre in eight small streams flowing from Walna Scar, at altitudes of 320 to 430 m. These streams all rise as small springs flowing from fissures in rocks near the surface. The high concentrations might be due to higher evapotranspiration in summer and extra unrecorded deposition of sea-salts in the lower part of the Duddon valley, although I believe this is unlikely as a complete explanation.

Chloride and sodium in surface waters on other rock-types

On the high fells comprised of SKIDS, the composition of streams and the few tarns on these rocks resembles that of waters on BORVS. However, at lower altitudes, especially below ca. 300 m, both chloride and sodium increasingly occur at higher concentrations, and there is a marked and significant difference between their concentrations in surface waters on BORVS and SKIDS (Fig. 4;
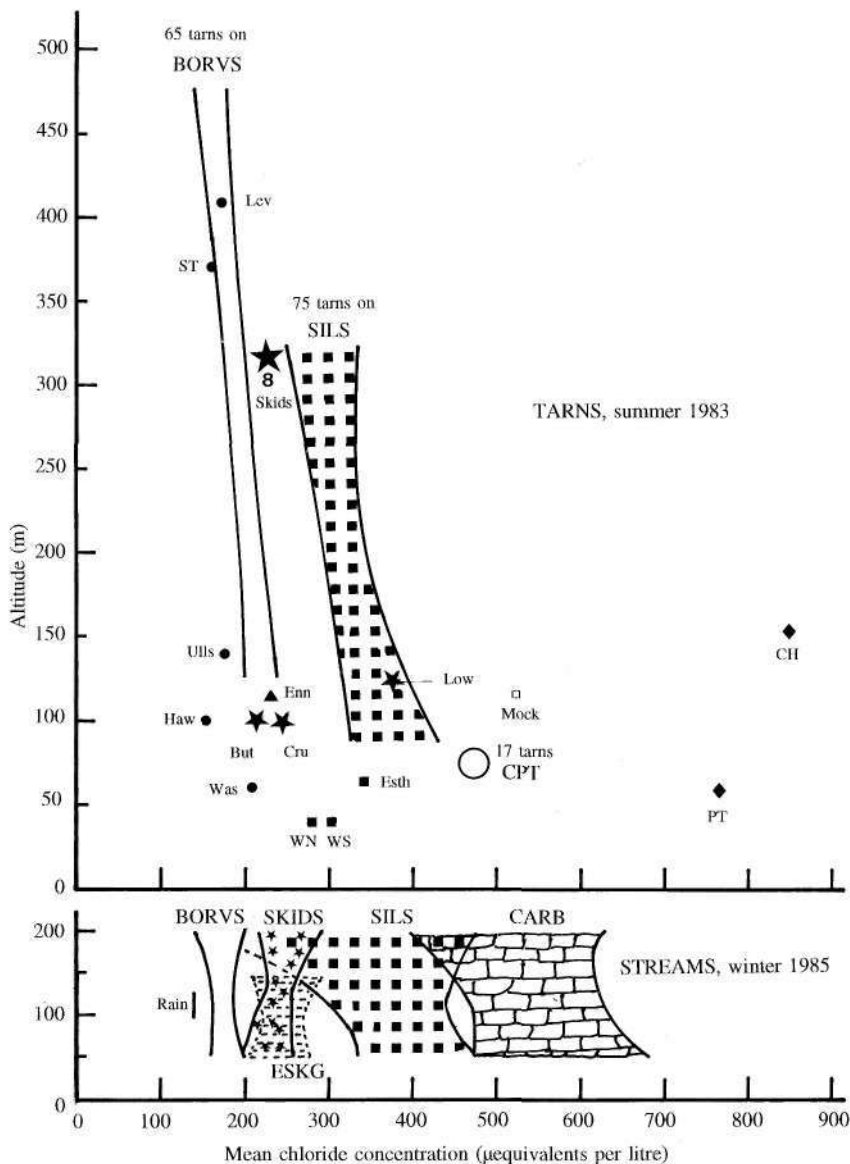
FIG. 4. *(On opposite page)* Mean concentrations of chloride (uequivalents per litre) related to altitude (metres above sea-level) and catchment geology for tarns in summer 1983 (above) and streams in winter 1985 (below); the curved lines are 95% confidence limits for mean values calculated from regressions of chloride versus altitude. Calculated mean chloride in streams on SKIDS and ENNG closely overlap, so do some values on SILS and CARB at 150-200 m altitude, where CARB represents streams on Carboniferous Limestone on the eastern fringes of the Lake District. Positions of lakes are shown for:- Leverswater (Lev), Seathwaite Tarn (ST), Ullswater (Ulls), Haweswater (Haw), Wastwater (Was) (circles, on BORVS); Buttermere (But), Crummock Water (Cru), Loweswater (Low) and eight tarns (asterisks, on SKIDS); Ennerdale Water (Enn) (triangle, on ENNG but draining BORVS); Windermere North (WN) and South (WS) Basins, Esthwaite Water (Esth) (squares, on SILS, but WN and WS drain BORVS); seventeen tarns (open circle, CPT in west and north Cumbria); Mockerkin Tarn (Mock) on the border of SKIDS and CPT; Parkgate Tarn (FT) and Chapelhill Tarn (CT) on lower ESKG.

Tables 2 and 3). On SKIDS, concentrations resemble those found on the igneous intrusions of ENNG, and ESKG in Upper Eskdale. Concentrations are particularly high on CPT in the lowland region surrounding the higher fells, where chloride and sodium are some two to four times higher than can be accounted for by mean atmospheric deposition, even when this is multiplied by 1.40. Waterbodies on SILS also have relatively high chloride and sodium concentrations, and Fig. 4 clearly shows that mean levels of chloride in surface waters at low altitudes are significantly different and characteristic for each of the major rock-types found in Cumbria. This fact makes it unlikely - indeed improbable - that the increasingly higher concentrations of chloride (and some other ions) are due solely or in major part to the concentration of atmospheric deposition by evapotranspiration. Possible sources of mineral-rich ground-waters) are proposed and discussed later.

Potassium, sulphate and nitrate on all rock-types

Winter concentrations of potassium in tarns and streams on the high fells are similar to a mean of 8-9 µeq per litre for deposition multiplied by 1.40, though in some instances winter concentrations are higher, perhaps due to input from potassium-rich rocks (Table 2). During summer, potassium in streams may be appreciably lower, even at low altitudes on BORVS, due to uptake by vegetation on the catchments. However, tarns on SKIDS had a mean concentration of 19 µeq per litre in the summer of 1983, and all waters on ESKG, SILS and CPT are relatively rich in potassium at all times of the year.

Sulphate concentrations generally are higher than the mean for deposition multiplied by 1.40 (i.e. 83 µeq per litre), though the increase is mostly small on BORVS, SKIDS and ENNG, especially in streamwaters compared with tarns. Some streams on ESKG are rich in sulphate, particularly in Lower Eskdale where iron pyrites is common in the rocks. All waters on SILS and CPT are rich in sulphate.

Table 4. Altitude (metres above sea-level), mean concentrations (microequivalents per litre) of several major ions in the 1970s and 1980s, and the ratios of sodium to chloride in selected Cumbrian lakes, related to the main bedrocks of the lake basins, f indicates lakes with part of the catchments lying on other bedrocks. (S) indicates saline input from Manesty saltwell into Derwentwater. * indicates non-marine (sea-salt) component for sulphate and potassium, calculated relative to chloride assumed to be wholly derived from the sea via atmospheric deposition. Lakes are also ranked from 1 to 18, representing increasing algal productivity assessed from a suite of variables measured in 1978 and 1984 (Kadiri & Reynolds 1993).

Lake	Alt	Cl⁻	Na/Cl	NO₃	*SO₄²⁻	*K⁺	Alk	Rank
Borrowdale Volcanics and igneous intrusions								
Levers Water	411	194	0.84	30	86	7	−18	–
Thirlmere	179	175	0.91	13	95	4	50	3
Brotherswater	173	197	0.99	12	137	5	188	9
Ullswater†	145	178	0.97	11	118	9	231	14
Ennerdale Water†	112	226	0.85	25	77	6	38	2
Haweswater	98	155	0.95	15	127	9	175	7
Grasmere	62	191	0.96	17	119	7	141	11
Wastwater	61	196	0.87	25	71	4	42	1
Rydal Water	53	200	0.97	13	115	8	156	10
Skiddaw Slates								
Buttermere†	101	219	0.78	13	66	4	40	5
Crummock Water	98	227	0.80	15	76	5	39	4
Derwentwater†(S)	75	298	0.74	8	79	4	98	6
Bassenthwaite Lake†	69	309	0.81	16	116	12	189	12
Loweswater	121	347	0.77	41	131	13	158	17
Silurian Slates								
Windermere NB†	39	266	0.83	28	117	10	191	13
Coniston Water†	44	259	0.85	22	157	10	178	8
Windermere SB†	39	283	0.83	29	120	11	224	15
Blelham Tarn	42	248	0.90	21	217	21	403	18
Esthwaite Water†	65	348	0.75	48	171	21	364	16

Nitrate concentrations in upland streams and tarns on BORVS are similar to annual deposition multiplied by 1.33 to 1.40, especially in winter when uptake by terrestrial and aquatic plants is expected to be minimal and nitrate concentrations in water are maximal. A relatively high mean winter concentration of 45 µeq per litre was found in the spring-sources of eight streams above 500 m altitude on the Shap Fells in Sleddale. Most waters on SILS and CPT are relatively rich in nitrates during winter, especially streams, where mean concentrations of more than 100 µeq per litre were obtained in winter 1985 (Table 2). These streams flow through lowland areas where agricultural runoff from improved grassland and some arable land contributes to the nutrient load.

When sampling, obvious point-sources of inputs were avoided (readily

identified by high potassium, nitrate and chloride) and water samples were usually obtained above farms. Nevertheless, uniformly high nitrate concentrations were found in streams draining unimproved grazing land on Carboniferous Limestone in the lower Lune Valley; these streams were also rich in potassium and chloride.

Major ions in the larger lakes

Mean concentrations of several ions are shown in Table 4. As mentioned earlier, Levers Water, Seathwaite Tarn and Wastwater, situated on BORVS, have means resembling that of measured deposition multified by a factor of 1.33 to 1.40, with the addition of calcium and Alk in the last two waterbodies. Thirlmere (a drinking-water reservoir) is also similar but nevertheless contains additional small inputs of chloride from road-salting in winter on the A591 highway over Dunmail Raise, as do Grasmere and Rydal Water; these last two small lakes also receive further additions of sodium, chloride and potassium from treated sewage. Brotherswater receives road-salt from the A592 highway on the Kirkstone Pass; so does Ullswater and hence (in recent years) Haweswater, a storage reservoir into which water from Ullswater is pumped to maintain water supplies further south.

Chloride in Ennerdale Water is noticeably higher than in other lakes on BORVS and ENNG (Table 2), although the principal inflow (River Liza) drains Great Gable and Green Gable on BORVS, and other inflows and the upper part of the lake basin lie on the local granophyre. However, the lower part of the basin is on SKIDS, where chloride concentrations in streams and tarns are generally some 30 to 40% higher. This extra chloride (balanced mainly by sodium and calcium) apparently raises the concentration of salt in Ennerdale Water which, in other respects, resembles the ionic composition of Wastwater in the adjoining catchment to the south. The particular influence of SKIDS is reinforced by the fact that rainfall sampled (regularly) in Ennerdale contained far less salt (ca. 64%) than the nearby lakewater.

Five other lakes on SKIDS also have relatively high salt concentrations (Table 4), especially Derwentwater which flows into and directly affects Bassenthwaite Lake; the former has an extra source of chloride from salt-rich groundwater associated with Manesty saltwell (Sutcliffe & Carrick 1983a). But Loweswater is the strangest of the five major lakes on SKIDS. In Loweswater the chloride concentration is as high as that of Esthwaite Water on Silurian Slates in the south of the Lake District (Fig. 4), and noticeably higher than chloride in other waters on SKIDS (Tables 3, 4 and Fig. 4). The ratio of Na/Cl is also low (0.77), resembling that of tarns and streams on SILS, and that of the chloride-rich Mockerkin Tarn which lies some 3-4 km west of Loweswater, on Carboniferous rocks adjacent to the western edge of the Loweswater catchment. In fact the ionic composition of the lakewater suggests there may be

some underground connection with groundwater in the rocks to the west, contrasting markedly with Cogra Moss - a tarn 3 km to the south-west of Loweswater - which also lies on SKIDS but has an appreciably lower chloride concentration (275 μeq per litre) and higher Na/Cl ratio (0.85).

Loweswater is also peculiar and enigmatic because it is relatively productive, ranked 17th amongst 18 major lakes in 1978-1984 (Table 4). Enrichment partly may be due to local agriculture, but the lake has a history of summer anoxia and high algal productivity extending back to medieval times (Pennington 1981). If a connection with groundwater from nearby Carboniferous rocks does exist, this water could also be a source of nutrients to Loweswater; surface waters on CPT are generally rich in nitrates, phosphates, potassium and calcium. Similarly, I suggest there might be enriched groundwater inputs to Ullswater, a lake of considerable volume and ranked 14th for productivity (Table 4) but, apparently, lacking the large and obvious nutrient inputs that contributed to recent increases in the productivity of Windermere and Esthwaite Water (George et al. 1990; Tailing 1993; Maberly et al. 1994; Heaney et al. 1996). Like Windermere, most of the major inflows to Ullswater predominantly drain high fells on BORVS, but the lake basin and surrounding lower parts of the catchment lie on the Eycott Group of sedimentary rocks, related to SKIDS, and several other rock-types are also present. Moreover the locality is criss-crossed by a series of major faults that have dislocated the bedrocks both vertically and horizontally; one (the Howtown Fault) is responsible for the sudden change in direction or "kink" half-way down the lake (Fig. 1), and the fault-lines could assist the movement of relatively deep groundwater in the rocks. The outflow (eastern) end of Ullswater abuts or actually lies on Carboniferous rocks.

On SILS in the southern part of the Lake District, all waterbodies tend to have relatively high chloride concentrations and low ratios of Na/Cl (Table 4). Once again this points to the existence of underground sources of water containing extra chloride that cannot be accounted for simply by atmospheric deposition and evapotranspiration on the catchments (Fig. 4).

Possible sources of ion-rich groundwaters in the Lake District

Two main sources of groundwaters rich in chloride and other ions are considered here: (1) relatively small amounts of water deep down in bedrocks on the upland fells, and localised in extent on each catchment; (2) more widespread and extensive waters deep underground in the sedimentary rocks surrounding the volcanic core of Lakeland.

On the high fells of BORVS and SKIDS, many of the streams begin as small trickles of water flowing from fissures in exposed bedrock. Although many of these apparently dry up during prolonged summer droughts, some water usually may be found by digging a few centimetres down into the streambed,

where invertebrates find a refuge. Some springs continued to flow, albeit somewhat feebly after a time, during the long hot summers of the mid-1970s. One such spring is Brownrigg Well, situated only 91 metres below the summit of Helvellyn (altitude 950 m). The spring produces water enriched with sodium, calcium and bicarbonate, making it suitable for pH-sensitive taxa such as the amphipod *Gammarus pulex* (Sutcliffe & Carrick 1973). Elsewhere, other springs are similarly enriched, including raised concentrations of chloride and potassium; some are acidic whereas others have remarkably high concentrations of calcium bicarbonate (alkalinity) (Sutcliffe & Carrick 1983b, 1988). The differences in chemical content of these springwaters must be due to prolonged contact with rocks of different chemical compositions, reflecting the complex nature of the slow-weathering bedrocks of the central fells.

The fact that springs continue to produce water during droughts indicates that subsurface and deeper bedrocks contain water that has percolated well down below the surface and near-surface saturated soil horizons. Presumably this deep groundwater moves through and is stored within numerous large and small fissures in the slaty bedrocks of BORVS and SKIDS; only gradually will it mix with the more abundant near-surface groundwater moving downhill. Testimony to the waterholding capacity of BORVS and SKIDS is provided by the numerous mining operations (for a wide variety of mineral ores) that flourished in Cumbria until the early part the 20th century (CATMHS 1992). Some of the old mine shafts extend into bedrock for 300 m or more in both the horizontal and vertical planes and, despite attempts to prevent or minimise the ingress of surface drainage, the mines required constant de-watering when in use!

I suggest that retention and contact-times for water held deep in the rocks may extend over periods of years and perhaps for decades or centuries, during which dissolution of ions from the bedrocks increases the concentrations of major basic cations. At the same time, some chloride may be derived from biotite, although the ratios of Na/Cl from this source are likely to exceed 1.0. Groundwaters in the UK can be held in rocks for long periods. An example is the thermal springwater at Bath - the Roman *Aquae Sulis* in the 1st century AD - where its medicinal and soothing properties were recognised and dedicated to the goddess Minerva, whilst fully acknowledging the more ancient presence of the Celtic goddess Sul. More prosaically, the water then as now flowed underground from a store held in the Carboniferous Limestone of the Mendip hills. This sulphurous water is only slightly brackish (sodium and chloride in equal amounts at ca. 8 milliequivalents per litre) but surprisingly has an estimated age of at least several thousand years (post-glacial) and may be much older, possibly dating from the last inter-glacial period (Andrews et al. 1982). Another example is saline groundwater originating deep in the Carnmenellis granite in Cornwall. Springs of warm water erupt in the old tin mines, at depths of 200 to 700 metres; the water is estimated to be ca. one million years old

Table 5. Concentrations of major ions (milliequivalents per litre) and ratios of four ions relative to chloride in saline spring-waters at Shap Wells on the eastern edge of the Lake District (data for 1888 from Aveline & Hughes), Manesty at the southwestern end of Derwentwater (data from Round 1960 and Sutcliffe & Carrick 1983a) and Brandlehow just north of Manesty (sampled twice in 1986). Sea water is included for comparison.

Ions	Shap Wells Spawater		Manesty Saltwell	Brandlehow		Sea water
	1888	1986	1953	July 1986	Aug 1986	
Na+	48	53.1	215	77.0	46.9	459
K+	–	2.0	2	1.4	1.0	9.7
Ca^{2+}	57	55.3	193	68.0	50.4	20
Mg^{2+}	1	0.3	22	4.8	2.3	104.6
Cl-	104	98.5	410	146.0	88.5	535.3
SO$_4^{2-}$	2	11.9	nil	2.0	1.3	55.2
NO$_3^-$	–	<1	nil	1.0	<1	–
Alk	–	0.2	–	0.3	0.52	2.3
pH	–	6.8	–	6.7	6.9	–
Na/Cl	0.46	0.54	0.52	0.53	0.53	0.857
Ca/Cl	0.55	0.56	0.47	0.47	0.57	0.037
Mg/Cl	0.001	0.003	0.05	0.03	0.03	0.195
SO$_4$/Cl	–	0.12	–	0.01	0.01	0.103

(Edmunds et al. 1984).

In Cumbria, there is firm evidence for the existence of mineral-rich groundwaters in low-lying sedimentary rocks surrounding the central core of BORVS. These spring to the surface in several places, e.g. Manesty and Brandlehow on the western shore of Derwentwater at ca. 75 m above sea-level, and Shap Wells at 213 m above sea-level, on the eastern side of the Lake District (Table 5). These localities lie on or are close to the geological boundaries between BORVS and other rock-types surrounding the central core of extruded lavas and granitic intrusions. At these boundaries, upward movement of water from considerable depths may be possible through fractured rocks and fault-lines. Water reaching the surface in the springs or "wells" has chlorinity values ranging from 17% to 77% of normal sea water but is clearly not derived from that source, as sodium is appreciably lower than would be expected (Table 5). Other ions also are enriched (barium, strontium) or depleted (magnesium, potassium, boron) relative to sea water (Hamilton-Taylor et al. 1988). In fact, the high chloride concentration is balanced by roughly equal concentrations of sodium and calcium ions (Table 5), as was noted first by Ransome (1848) who examined a sample of strongly saline water from the ancient lead mine at Brandley or Brandlehow, close to the Manesty saltwell. Ransome's analytical results were reproduced by Postlethwaite (1889). He describes an adit level or "salt level" and a saline spring in the Brandlehow mine, both at lake-level. Mining operations (for galena, cerussite,

blende, iron pyrites, manganese and sulphate barytes, and small amounts of gold) in the 18th and 19th centuries eventually required pumps to remove the saline water from depths of 60 fathoms (360 ft or ca. 110 m) and more, well below the maximum depth of water in the lake (22 m) and below the level of the immediate post-glacial rock-bed of Derwentwater; in fact, also below the surface-level of the Irish Sea. [A rough calculation indicates that pumped saline water entering the well-flushed lake (volume 29×10^6 m^3 and retention time ca. 55 days) would raise the latter's salinity by relatively small amounts; the lakewater would not have been "brackish"!].

Nevertheless the chloride concentration of Derwentwater is relatively high (Table 4) and ca. 27% can be attributed to the net effect of saline groundwater in the vicinity of the lake, including that rising in the Manesty saltwell. This saline spring, known for centuries, was used locally for medicinal purposes (Kipling 1953; Table 5) but is now difficult to find and appears to have stopped flowing.

Chemical analysis of pore waters in two sediment cores taken from Derwentwater shows that there are diffusion-controlled concentration gradients of elements in the lake sediments. These increase with depth, indicating a hydraulic connection with a reservoir of highly saline water which, on evidence from analyses of the stable isotopes of oxygen and hydrogen, appears to result from rock-water interactions that may have occured through considerable periods of time, possibly spanning the last million years although much shorter time-spans cannot be ruled out (Edmunds et al. 1985; Hamilton-Taylor et al. 1988). The interactions may involve the hydrolysis of biotite, K_2 $(Mg, Fe)_4'(Fe, Al, Li)_2$ $[Si_6 Al_2 O_{20}]$ $(OH)_2$ $(F, Cl)_2$, within the local granite and yielding chloride in quantity. Major contributions of sodium and calcium may occur from the acid hydrolysis of plagioclase feldspar (Edmunds et al. 1984, 1985).

Concluding remarks

Differences in composition of major ions and their concentrations in the surface waters of Cumbria reflect the complex geological structure of the region. At altitudes above 300 m, on BORVS and SKIDS, surface waters are qualitatively and quantitatively derived from atmospheric precipitation, with additional inputs of some ions - especially calcium and bicarbonate - from catchment rocks and soils. In some of the low-lying large lakes on the fringes of the central fells, water composition is also dominated by inputs from the upper catchments on BORVS; examples are Wastwater, Ullswater and Haweswater. However, in other lakes there is direct evidence (Derwentwater and Bassenthwaite Lake) or clear indirect evidence (Loweswater) of inputs from saline groundwater rich in sodium and calcium chloride. Saline groundwater also appears to affect other low-lying lakes on sedimentary rocks,

though its presence is largely obscured by mixing with dilute water from the upper catchments; examples are Ennerdale Water, Buttermere, Crummock Water, Coniston Water, Windermere and, possibly, Ullswater. Many streams on sedimentary rocks (SILS and CPT) at altitudes below 300 m are unaffected by dilution from higher catchments, and these streamwaters display evidence of inputs from saline groundwater in addition to major inputs from local rocks and soils. Sea water is unlikely to be the source of this extra salinity which, it is suggested, may be derived from water-rock interactions involving the underlying granite batholith, followed by upward movement into the overlying sedimentary rocks. The latter are relatively thin, being only a few hundred metres thick, especially near the boundaries with the extruded granites.

The above facts and speculative arguments point to the need for more extensive and detailed geochemical studies on the Lake District rocks and associated groundwaters, including water in the deeper parts of old mines. Such research is essential for a better understanding of a complex series of phenomena that could have important implications for the movements of water and elements within lake sediments and the bedrocks of their basins, and also between adjoining rock-strata. A revision of the permeabilities of local bedrocks, especially the granites (Patrick 1978), and the role of the underlying granitic batholith (Lee 1986), is also required. One point is demonstrably clear: chloride concentrations provide a valuable baseline for some purposes when estimating budgets for water and elements, but the assumption that it is truly conservative and derived only from deposition on the catchments is not universally true, and can introduce substantial errors when applied away from the central upland areas of the Lake District.

Finally, in this article I have described the observed similarities and differences between the ionic compositions of waterbodies on the major rock-types in Cumbria, given some emphasis to the overall relationship between altitude and chloride concentrations, and speculated on the existence of chloride-rich groundwaters that may provide at least partial explanation for the notable elevation of chloride in surface waters at low altitudes. I have not attempted to provide explanations for the equally notable differences that exist between waterbodies at similar altitudes on the major rock-types, which are summarised in Fig. 4. Separate sources of chloride-rich groundwater, differing degrees of dilution with surface water, the permeabilites of major rock-strata and the relative depths of the underlying granite batholith, are factors that may be important and require more detailed examination in future studies.

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