


Carbon-13 in groundwater from English and Norwegian crystalline rock aquifers: a tool for deducing the origin of alkalinity?

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Abstract The ¹³C signature is evaluated for various environmental compartments (vegetation, soils, soil gas, rock and groundwater) for three crystalline rock terrains in England and Norway. The data are used to evaluate the extent to which stable carbon isotopic data can be applied to deduce whether the alkalinity in crystalline bedrock groundwaters has its origin in hydrolysis of carbonate or silicate minerals by CO₂. The resolution of this issue has profound implications for the role of weathering of crystalline rocks as a global sink for CO₂. In the investigated English terrain (Isles of Scilly), groundwaters are hydrochemically immature and DIC is predominantly in the form of carbonic acid with a soil gas signature. In the Norwegian terrains, the evidence is not conclusive but is consistent with a significant fraction of the groundwater DIC being derived from silicate hydrolysis

by CO₂. A combined consideration of pH, alkalinity and carbon isotope data, plotted alongside theoretical evolutionary pathways on bivariate diagrams, strongly suggests real evolutionary pathways are likely to be hybrid, potentially involving both open and closed CO₂ conditions.

Keywords CO₂ sink · Carbonate · Silicate · ¹³C isotope · Groundwater · Granite

Introduction

Hydrogeochemistry, alkalinity and the global CO₂ sink

Relatively little recent discussion has taken place in the scientific literature regarding the evolution of carbonate alkalinity in groundwater in crystalline silicate bedrock aquifers, such as granites, gneisses, basalts, dolerites, and schists. Despite the relatively low yields obtained from most such aquifers (Banks et al. 2010), they often form an important component of rural potable water supply in areas underlain by ancient shield terrane (Fennoscandian shield, Canadian shield, African shield) and the cores of orogenic belts (the Caledonides of Norway, Sweden and Scotland, the Hercynides of SW Britain and the Alps).

The accumulation of alkalinity in groundwater in such aquifers is intimately linked to the evolution of pH, a master variable which often controls the solubility of other trace elements that may have health-related significance (Frengstad et al. 2001; Appelo and Postma 2005).

Additionally, however, the enrichment of alkalinity in groundwater is an indicator of the consumption of carbon dioxide in mineral weathering and, thus, offers insights into the magnitude of the global sink for atmospheric carbon that mineral weathering represents. Several authors (e.g. Banks

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and Frengstad 2006; Schulte et al. 2011) have suggested that ^{13}C stable isotope determinations might (“**Implications for bedrock weathering as a global CO₂ sink**”, “**Carbon isotope fractionation in the groundwater recharge process**”, “**Hypothetical groundwater ^{13}C signatures in carbonate and silicate weathering systems**”) be able to indicate whether this alkalinity is derived from silicate or carbonate weathering and, thus, whether it represents a permanent or temporary CO₂ sink. This paper presents data on ^{13}C in several different environmental “compartments” (vegetation, soil gas, soils and groundwater) from three different English and Norwegian crystalline bedrock areas. It uses the data to ascertain whether this hypothesis can be readily applied in practice to ascertain if groundwater alkalinity is derived primarily from carbonate weathering (temporary CO₂ sink) or silicate weathering (permanent CO₂ sink).

Hydrogeochemical evolution in crystalline bedrock aquifers

A typical evolution of groundwaters in crystalline bedrock aquifers in boreal and temperate climates appears to follow a pathway comprising four broad ‘phases’ (Frengstad and Banks 2007):

Phase (i) Hydrochemically immature waters. Low pH and alkalinity, cationic and anionic composition still characterized by evapo-concentrated components of rainfall.

Phase (ii) Gradual enrichment of base cations and alkalinity in groundwater, typically calcium and bicarbonate. Circum-neutral pH.

Phase (iii) Preference for accumulation of sodium and bicarbonate. As pH increases to alkaline values, apparent depletion of calcium to leave a high-pH sodium bicarbonate water.

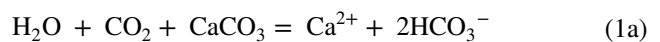
Phase (iv) At greater depth and prolonged residence time, deep brines (Gascoyne and Kamineni 1993; Bottomley et al. 1990) of sodium/calcium sulphate/chloride composition.

Banks and Frengstad (2006) noted that water types representing Phases (i) to (iii) could be found in shallow Norwegian crystalline bedrock aquifers, even in relatively simple aquifer lithologies such as anorthosite (Table 1), which is dominated by plagioclase feldspar. It seems reasonable that groundwaters in Phase (i) represent newly recharged water, with very little rock-water interaction and containing evapo-concentrated rainfall solutes. The evolution to Phase (ii) represents the accumulation of base cations (especially calcium and bicarbonate) by the relatively rapid hydrolysis of carbonate minerals, such as calcite (Eq. 1a), and, to some extent, kinetically slower hydrolysis of silicate minerals. Calcite and other carbonates may be present in soils or recent superficial deposits overlying the crystalline bedrock aquifer, or they may be present as trace components

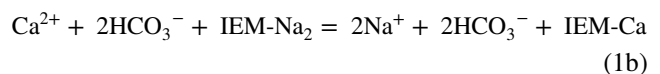
Table 1 Three characteristic groundwater analyses from the Egersund anorthosite massif, Norway, ranging from Phase (i) evapo-concentrated recharge water, dominated by Na and Cl from rainfall recharge, to Phase (iii) high pH, Na-HCO₃ water, depleted in calcium. Data from Banks and Frengstad (2006)

Sample		2	5	8
Phase		(i)	(ii)	(iii)
Eh	mV	+260	+171	+70
pH		5.59	7.90	9.72
Alkalinity	meq/L	0.2	2.2	3.0
Na ⁺	mg/L	20.5	40.7	83.2
Ca ²⁺	mg/L	7.86	40.9	2.49
Mg ²⁺	mg/L	4.02	16.3	0.97
K ⁺	mg/L	2.16	3.11	0.63
Cl ⁻	mg/L	34.2	18.1	30.9
SO ₄ ²⁻	mg/L	13.9	33.9	12.1
NO ₃ ⁻	mg/L	12.5	127	<0.05
F ⁻	mg/L	<0.05	0.06	0.07
Si	mg/L	2.06	3.41	4.16

or fracture surface minerals within the crystalline bedrock lithology itself (White et al. 1999, 2005).

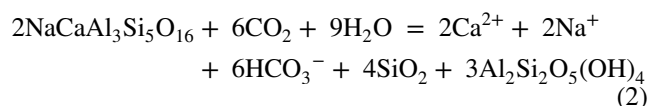


Many hydrogeologists explain the transition from Phase (ii) to Phase (iii) by ion exchange of sodium for calcium. The removal of calcium also increases calcite undersaturation and, thus, potentially allows the further dissolution of calcium carbonate and accumulation of alkalinity (Eq. 1b; Model A).

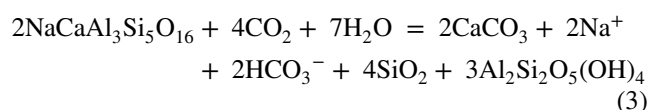


where IEM is an ion exchange medium (e.g. a clay).

Frengstad and Banks (2000) and Banks and Frengstad (2006) posited the alternative explanation (Model B) that Phase (iii) represents the gradual predominance of kinetically slower hydrolysis of abundant silicate (e.g. plagioclase feldspar) phases by dissolved carbon dioxide (Eq. 2).



Banks and Frengstad (2006) explained the depletion in calcium and evolution of groundwaters to very high pH values by the progressive precipitation of calcite as alkalinity accumulates from silicate hydrolysis (Eq. 3).



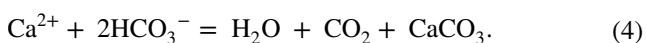
Frengstad and Banks (2007), while recognising that carbonate dissolution and ion exchange may be important processes in many specific cases, argued that silicate (often dominated by feldspar) hydrolysis alone can explain most of the main hydrochemical trends observed in groundwaters from silicate crystalline rocks. They contended [by merely extending the evolutionary principles first proposed by Garrels (1967) and Garrels and MacKenzie (1967)] that these trends are not strongly dependent on lithology, but are dependent on five more universal factors; (1) the initial partial pressure of CO₂ (PCO₂) of the recharge water, (2) the degree to which the aquifer geochemical system is “open” or “closed” with respect to CO₂, (3) the availability and composition of hydrolysable silicate phases, (4) the degree to which CO₂ has been consumed by silicate (e.g. plagioclase) hydrolysis and (5) the extent to which silicate hydrolysis has continued beyond the point of calcite saturation.

Implications for bedrock weathering as a global CO₂ sink

In the context of greenhouse gas-coupled climate change it is important to understand and quantify the various available CO₂ sources and sinks globally. One, often under-recognized, potential sink is the consumption of CO₂ by weathering of carbonate, aluminosilicate and other basic minerals in the subsurface (Brady 1991; Liu and Zhao 2000; Probst et al. 1998; Gaillardet et al. 1999; Amiotte-Suchet et al. 2003; Beaulieu et al. 2012). Especially in the boreal regions of the globe, the terrain is underlain by large areas of glaciated shield terrain where relatively fresh crystalline bedrock mineral assemblages have been recently exposed (Canada, Fennoscandia, Greenland, parts of Russia and Siberia).

Note that, in Model A, the groundwater’s alkalinity is derived from carbonate hydrolysis, in which case, half of the resultant alkalinity in groundwater is derived from mineralogical fixation of atmospheric/soil-produced CO₂ (Eqs. 1a, b).

In Model B, the alkalinity is derived from silicate hydrolysis, in which case, all the resultant alkalinity in groundwater is derived from mineralogical fixation of atmospheric/soil-produced CO₂ (Eqs. 2, 3). This has obvious implications for scientists attempting to quantify the degree to which mineral weathering acts as a global sink for CO₂. Of course, if the groundwater discharges to a surface or ocean water, calcite may be precipitated, re-releasing CO₂:



If this is taken into account, the net mineralogical fixation of CO₂ in Model A might be as low as zero, while in Model B it would be no lower than 50%.

The methods, based on ¹³C characterisation of groundwater dissolved inorganic carbon (DIC), described in this paper potentially allow us to distinguish between the two models for groundwater alkalinity generation and, hence, to refine our estimates of the magnitude of the mineralogical CO₂ sink.

Carbon isotope fractionation in the groundwater recharge process

Atmospheric carbon dioxide has a typical δ¹³C of –6 to –8‰ (Cerling et al. 1991; see also Craig 1953). As this carbon is photosynthesized by plants and incorporated into plant tissue, it undergoes a fractionation, depending on the metabolic pathways of the plant in question. C3 metabolic pathways (including most temperate plant species) result in a δ¹³C composition in the range –20 to –40‰ (Staddon 2004), but most typically –24 to –30‰ (Clark and Fritz 1997).

As plant material decays and soil is formed, this signature is broadly preserved, with a bulk soil organic δ¹³C of –23 to –30‰ being typical for temperate climates. The biota living in such soils generally exhibit a +1–2‰ differential relative to the bulk soil.

Plant roots and some soil biota respire CO₂, while other soil organisms degrade soil organic matter by heterotrophic microbial oxidation (Gillon et al. 2012). Root-respired CO₂ is similar to the bulk plant root δ¹³C composition, while degradation-derived CO₂ is typically slightly depleted in ¹³C. The “biologically-produced soil CO₂” thus has a δ¹³C signature slightly lower than the plants and the bulk soil, at around –32 to –27‰.

This “biologically-produced soil CO₂”, however, is not necessarily identical to the bulk soil gas CO₂ signature, the latter being affected by diffusion of soil CO₂. As isotopically lighter ¹²CO₂ diffuses faster, the soil gas δ¹³C signature is heavier than that of the “biologically-produced soil CO₂”, and increases upwards in the soil profile, as the soil-atmosphere interface is approached. The higher the soil respiration/degradation rate, the lighter the soil gas δ¹³C signature will be. Irrespective of this rate, at some depth within the soil profile, a steady state δ¹³C signature will be achieved which, in well-drained soils, is normally +4.4‰ higher (heavier) than the biologically produced signature (Cerling 1984; Cerling et al. 1991, while Dörr and Münnich 1980; Alpers et al. 1990, discuss other factors that may affect this signature). Thus, at depth, a soil gas CO₂ signature of –27.5 to –23‰ is typical in temperate regions, dominated by C3 plants (as is the case for the three study areas). These processes are summarized in Fig. 1. It should be noted that, as biological productivity varies strongly seasonally (being highest in summer; Atkinson 1977, Qi et al. 2002), one

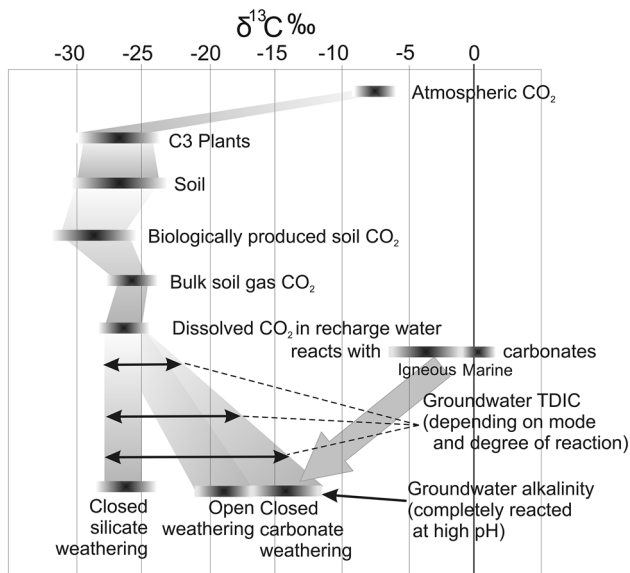


Fig. 1 Diagrammatic idealized representation of evolution of $\delta^{13}\text{C}$ signature in a typical temperate soil/soil gas/groundwater system. Ocean water has a $\delta^{13}\text{C}$ of around 0‰. The grey shading shows speculative ranges of isotopic signature, but founded in commonly observed values, as documented in “Carbon isotope fractionation in the groundwater recharge process” and “Hypothetical groundwater 13C signatures in carbonate and silicate weathering systems”

might expect the soil gas $\delta^{13}\text{C}$ signature to also vary with season and with weather/barometric conditions.

The soil gas CO_2 dissolves in recharge water (with a very modest associated $\delta^{13}\text{C}$ fractionation of c. -1‰ —Szarán 1998; Clark and Fritz 1997) and, either in the unsaturated or saturated zone, may react with basic mineral phases (carbonates or silicates etc.), resulting in a pH rise and an accumulation of bicarbonate or carbonate ions and base cations in the water [see Model A (Eqs. 1a, b) and Model B (Eq. 2)].

The equilibrium transition from dissolved $\text{CO}_{2(\text{aq})}$ to HCO_3^- is associated with a rather strong $\delta^{13}\text{C}$ fractionation of $+10$ to $+11\text{‰}$ (Mook et al. 1974; Clark and Fritz 1977). The further equilibrium transition to CO_3^{2-} is associated with a further fractionation of -0.4 to -0.6‰ . If the groundwater becomes saturated with respect to calcite and some degree of calcite precipitation occurs (Eq. 3), a further modest ($<2\text{‰}$) fractionation may be observed

(Emrich et al. 1970). Thus, in an equilibrated (open with respect to an effectively unlimited reservoir of CO_2) system, characterised by a soil gas of $\delta^{13}\text{C} = -26\text{‰}$, one would expect the ^{13}C signatures presented in Table 2.

Hypothetical groundwater ^{13}C signatures in carbonate and silicate weathering systems

In a purely silicate weathering system (Model B, above), the hydrolysis of silicate minerals raises the groundwater pH, converting dissolved $\text{CO}_{2(\text{aq})}$ to HCO_3^- and, at higher pH, to CO_3^{2-} .

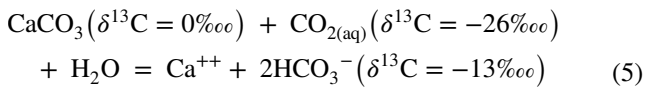
In a closed silicate weathering system, where the mineral assemblage has access to an initial finite dissolved CO_2 content, the overall $\delta^{13}\text{C}$ of the groundwater dissolved inorganic carbon (DIC) remains unchanged at the initial $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ value. As weathering progresses, the distribution of the species ($\text{CO}_{2(\text{aq})}$, HCO_3^- and CO_3^{2-}) comprising the DIC will shift to the right, but the total DIC will remain constant (at least, until saturation with respect to a carbonate mineral occurs, at which point a small fractionation may take place on precipitation—Emrich et al. 1970).

In an open silicate weathering system, the groundwater constantly has access to an unlimited supply of soil gas carbon dioxide to replace that converted to bicarbonate by mineral hydrolysis and pH increase. At any given point, the speciation of DIC will depend solely on pH and can be calculated. By assigning values of $\delta^{13}\text{C}$ to each species (as in Table 2, for example), the total $\delta^{13}\text{C}$ of the DIC can be calculated. As pH rises and a greater proportion of the DIC is in the form of HCO_3^- or CO_3^{2-} , the $\delta^{13}\text{C}$ of the DIC becomes isotopically heavier.

In a carbonate weathering system (Model A), one might expect the soil gas-derived CO_2 (highly negative $\delta^{13}\text{C}$) to be “diluted” by dissolution of aquifer carbonate (which typically has a $\delta^{13}\text{C}$ close to 0‰, if marine-derived). In a closed carbonate weathering system, this is indeed the case and, once the finite quantity of dissolved soil-derived CO_2 has fully reacted with aquifer carbonate, an intermediate $\delta^{13}\text{C}$ should result (Schulte et al. 2011—see Equations 1). For example, if the dissolved soil-derived CO_2 has a $\delta^{13}\text{C} = -26\text{‰}$, one would expect the DIC $\delta^{13}\text{C}$ to tend towards -13‰ .

Table 2 Fractionation, at 10 °C, of $\delta^{13}\text{C}$ signature in the aqueous carbonate system in equilibrium with an effectively unlimited gaseous carbon dioxide reservoir of signature $\delta^{13}\text{C} = -26\text{‰}$ (i.e. open system). (Values from Clark and Fritz 1977)

	$\text{CO}_{2(\text{gas})}$	\leftrightarrow	$\text{CO}_{2(\text{aq})}$	\leftrightarrow	$\text{HCO}_3^-_{(\text{aq})}$	\leftrightarrow	$\text{CO}_3^{2-}_{(\text{aq})}$
Fractionation							
Total fractionation from $\text{CO}_{2(\text{gas})}$							
Signature	-26‰		-27.1‰		-16.4‰		-16.8‰



In a truly open carbonate weathering system, the speciation of DIC and its $\delta^{13}\text{C}$ depend only on pH. Thus, in an idealised open system, the evolution of the $\delta^{13}\text{C}$ of DIC is the same as for silicate weathering and the “isotopic composition of the dissolved carbonate rock does not influence the $^{13}\text{C}/^{12}\text{C}$ ratio of the carbonate in solution” (Deines et al. 1974). In reality, of course, isotopic exchange between the dissolved and gaseous species may not be perfect nor instantaneous and a given CO_2 system may be in some way “intermediate” between the idealised open and closed situations.

The suggestion made by authors such as Banks and Frengstad (2006) and Schulte et al. (2011)—namely that ^{13}C isotopic signatures could potentially be used to distinguish between silicate and carbonate weathering (Models A and B)—is potentially a powerful one. However, although it would appear that $\delta^{13}\text{C}$ could be used to distinguish closed system silicate and carbonate weathering, there is no clear isotopic distinction between purely (ideal) open CO_2 weathering pathways.

To attempt to ascertain the practical utility (if any) of ^{13}C in resolving such issues, samples of vegetation, soils, soil gas and groundwater DIC were collected from three different crystalline bedrock terrains: the granitic Scilly Isles

of south-west England, the Iddefjord granite of south-east Norway and the Egersund anorthosite complex of south-west Norway. The last-named terrain is specially selected, as it comprises a simple mineralogy (dominated by plagioclase feldspar) with very little superficial cover, thus potentially minimising the impacts of carbonate mineral weathering in either the bedrock or overburden.

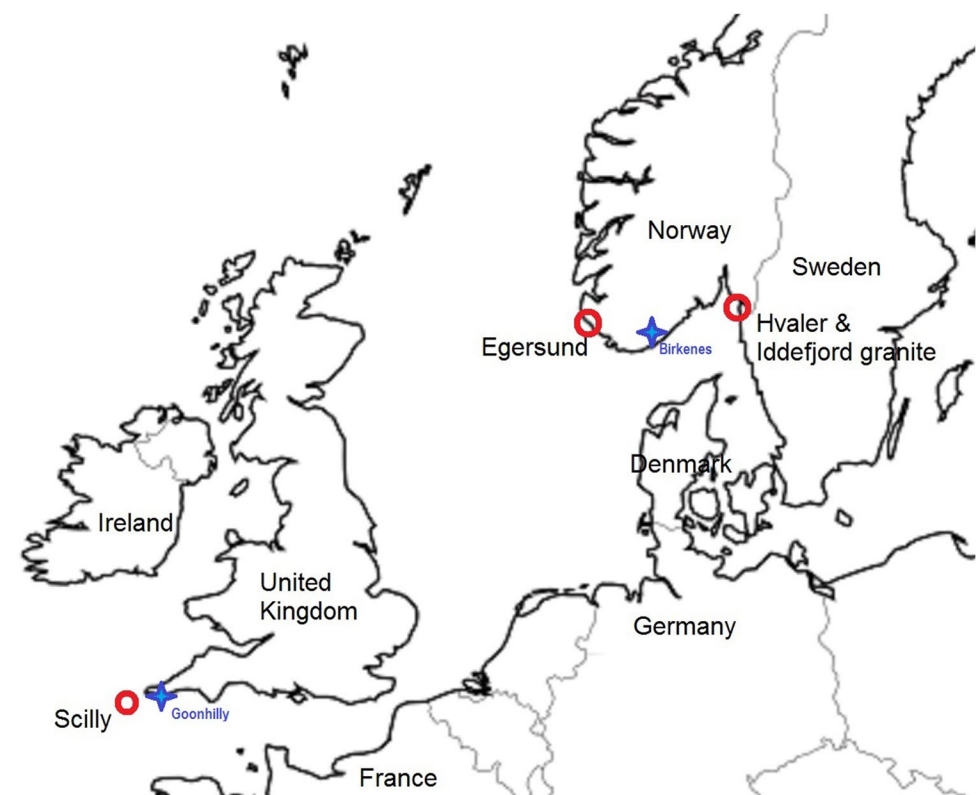
The study areas

Egersund anorthosite complex, Rogaland County, Norway

Egersund is situated in the county of Rogaland, southeast of Stavanger on the south-western coast of Norway (Fig. 2). The sampled area is underlain by the Precambrian Egersund-Ogna anorthosite massif which was emplaced into the Sveconorwegian orogenic belt at 931 ± 3 Ma (Schärer et al. 1996). The anorthosite typically comprises 90% coarse-grained plagioclase crystals (An40–50), with subsidiary Al-orthopyroxene, the whole being intruded by dolerite dykes (Ashwal 1993).

The terrain is dominated by extensive freshly glacially scoured and striated bedrock exposure. In coastal areas and below the level of the postglacial upper marine limit (PGUML), marine silts and clays (whose pore water

Fig. 2 Map of north-western Europe, showing the locations of the three study areas as red circles (Scilly, Egersund and Hvaler–Iddefjord). Also shows named rainfall stations as blue stars



provides a potential source of marine salts to groundwater occur in lower-lying terrain. These may be overlain in valleys by glaciofluvial and alluvial sands and gravels, which also occur in limited valley deposits above the PGUML. Postglacial isostatic uplift is of the order of 15 m (Norges geologiske undersøkelse 2014). Topography inland is relatively steep and soil cover is typically absent or very thin, except in local valley areas or under well-established forest areas. The annual average temperature is slightly over 7 °C at sea level and the maximum tidal range is only some 0.5 m. The annual precipitation is around 1540 mm (1971–2000; Norsk Klimaservicesenter 2017a). The potential evapotranspiration is around 450 mm (HydroTeamRC 2015).

The area is within the Boreal belt (Sundseth 2009), dominated by C3 processing plant pathways, an important control on the isotopic composition of the stable carbon contained within soil gas CO₂. Banks and Frengstad (2006) recorded CO₂ concentrations of 1–3.4 vol.% (PCO₂ 10^{-1.47} to 10⁻² atm.) in soil gas in the Egersund anorthosite area. Vegetation consists of scrub and low trees, including aspen, bilberry, birch, spruce, juniper, oak, pine, grasses and mosses.

The Hvaler Islands and surrounding area: Iddefjord Granite, Østfold County, Norway

The Iddefjord Granite outcrops in the southern region of Østfold County, Norway. It continues across the Swedish border, where it is referred to as the Bohus Granite. As well as the mainland areas around Fredrikstad and Halden, the granite also forms the popular holiday archipelago of the Hvaler Islands. The Iddefjord Granite of Hvaler is arguably one of the most-studied bedrock aquifers of Norway (Banks et al. 1992a, b, 1993a, b, 1994). The islands are an emergent landscape, having been exposed from the Skagerrak by postglacial isostatic uplift during the past 10,000 years. The islands have some pastoral and arable agricultural activity, but are also characterised by many holidaymakers' cottages.

According to Oxaal (1916), the Iddefjord Granite derives from the end of the Sveconorwegian orogeny (981 ± 7 Ma) and comprises 13 magmatic intrusions ranging from diorite to granite in composition, intruded into Precambrian gneiss country rocks. The granites are characterised as 'S type' (sedimentary origin) and are typically medium grained with c. 71–75% SiO₂ content and composed of quartz, microcline and plagioclase with accessory biotite, hornblende, muscovite, iron oxides, chlorite, apatite, titanite and zircon. The granite was subsequently intruded by dolerite dykes, some of which are deeply eroded and glacially "plucked". Many granite fractures are filled with smectite mineralization (Kocheise 1994), and other observed fracture minerals include chlorite, fluorite, epidote and calcite. Some of

this mineralization may be related to Permian hydrothermal activity associated with the Oslo Rift (Oxaal 1916; Holte-dahl 1960; Pedersen and Maaløe 1990; Banks et al. 1993b, 1994, 1997).

The terrain is dominated by extensive freshly glacially scoured and striated bedrock exposure. In coastal areas and below the level of the PGUML (which is at around 170 m asl—Selmer-Olsen 1964), marine silts and clays occur. Especially in the low-lying Hvaler islands, extensive deposits of shallow marine and littoral silts and sands are observed. Quaternary sedimentation also occurs within the eroded fracture zones of the granite terrain. A major terminal moraine train from the last deglaciation of Oslofjord can also be found. The annual average temperature is over 7 °C at sea level and the maximum tidal range is only some 0.5 m.

The location is within the Boreal C3 belt. Vegetation consists of scrub and trees, including aspen, bilberry, birch, hazel, heather, juniper, oak, pine, rowan, willow, spruce, umbellifers, grasses and mosses. Despite its extensive fresh granite surface exposure, large areas of low-lying Hvaler have a thin cover of Quaternary marine drift including some shell sand, well-developed vegetation and a consequent thick acidic organic soil layer. The annual precipitation is around 755 mm (1971–2000; Norsk Klimaservicesenter 2017b). The potential evapotranspiration is around 600 mm, of which around half is actual evapotranspiration (HydroTeamRC 2015; SMHI 2017).

The Scilly Isles, Cornwall, UK

The Scilly Isles are a granite archipelago in the Atlantic Ocean some 45 km WSW from Lands End, Cornwall (Barrow and Flett 1906). The islands form an extension of the Permo-Carboniferous (300–275 Ma) Cornubian Batholith of SW England (Osman 1928; Chen et al. 1993), comprising 'S-type' granitic intrusions, associated with the end of the Variscan orogeny. The granites are peraluminous with a low Na/K ratio, and enriched in Li, B and U. Two separate intrusions can be recognised in the Scillies, (1) the older coarse-grained Outer Granite forming St Marys, St Martins and much of St Agnes islands (into which the sampled boreholes have been drilled), subsequently intruded by (2) the medium-grained Inner Granite (Jones 1963). The granites comprise quartz, perthitic K-feldspar, oligoclase plagioclase (the feldspars often being porphyritic), lithium-rich biotite and muscovite (Stone and Exley 1989; Banks et al. 1998). Accessory minerals include tourmaline, iron oxides, apatite, zircon, andalusite, rutile, monazite, anatase, topaz, chlorite and brookite.

The Scilly Isles represent a submergent landscape, having formed a larger coherent island mass at the end of the last ice age (10,000 years BP). The question of whether (and when) Scilly experienced Pleistocene glaciation

is still debated, but it seems likely that, during the last glacial maximum, the bulk of the islands were unglaciated, and would have experienced periglacial conditions (Watkins 2000; Mitchell and Orme 1967; Hiemstra et al. 2006). The islands have thus (unlike Hvaler) experienced a geologically long history of sub-aerial weathering. The granite surfaces are seldom fresh and are often covered by a “head” or “ram” (slope-creep) deposit that in many ways resembles a tropical granite weathering layer or regolith. Other superficial deposits are sparse, although limited tracts of clayey alluvium occur in some areas, especially around Old Town on St Marys. Sea level rises (2.1–2.6 mm/year during the archaeologically datable period) following the last glaciations resulted in the inundation of Scillonia and its separation into the current islands maybe as late as 1000–1500 years BP (Ratcliffe 1992).

The tidal range is high (sometimes exceeding 5.5 m), while the annual average temperature is almost 12 °C. The annual average precipitation is 865 mm (St Mary’s Heliport, 1981–2010, Met. Office 2017) while the potential evapotranspiration over well-watered grass is around 526 mm/year (Land’s End, 2007–2012, CHES 2017). The islands host arable and pastoral agriculture and are particularly known for their winter floriculture, due to the mild climate. In recent years, tourism has become dominant as the main source of income. Vegetation includes large expanses of maritime heathland and grassland, with higher ground being occupied by bracken, gorse, heather and rhododendron. Wooded areas (e.g. pine) are scarce, occupying valleys in inland areas of the islands.

Previous comparative study

Banks et al. (1998) specifically compared the groundwaters of the Hvaler (Iddefjord Granite) and Scilly island groups. They found that the Hvaler groundwaters were typically hydrochemically rather mature (although a significant range was observed), with slightly alkaline pH, high alkalinity and high concentrations of fluoride, radon, uranium and non-marine (lithologically derived) sodium. Concentrations of nitrate were generally low, probably reflecting the lack of winter agriculture on the islands. The Scilly groundwaters, by contrast, were hydrochemically immature, with low pH, alkalinity, fluoride, uranium, radon, calcium and lithologically-derived sodium. Potassium and nitrate were typically rather high, reflecting the leachable nature of the soils and the winter agriculture and floriculture (Fig. 3). Banks et al. (1998) speculated that the differences were due to the most reactive components of the Scilly granite matrix and fracture mineral assemblage having been depleted during the long

history of subaerial weathering. At Hvaler, the reactive components of the mineral assemblage are still largely intact, following glacial scouring and marine emergence.

Field methodology

This paper is based on three studies of carbon isotopes in the vegetation/soil/groundwater system carried out during 2011–2012.

Study 1 Sampling of soil gas, rock and groundwater from the Egersund and Iddefjord granite areas during 27th June to 1st July 2011.

Study 2 Sampling of soil gas, vegetation, soils, superficial deposits and rock from Egersund and Iddefjord granite areas during 18th to 22nd June 2012.

Study 3 Sampling of soils, rocks, plants, soil gas and groundwater from the Scilly Isles during 18th to 22nd September 2012.

Groundwater samples

Sampled wells and boreholes were typically private sources in regular use and were, therefore, pumped regularly. There was thus generally little need to purge the wells prior to sampling. Samples were typically taken after allowing the sampling tap to run for several minutes. At each site, field determinations were made of pH (using an appropriately calibrated pH electrode) and total alkalinity, by means of a Hach digital titrator, using 1.6N H₂SO₄ and an indicator of end-point pH c.4.5. Groundwater samples were collected only in the course of studies 1 and 3; the following sample aliquots were collected in polyethylene (PE) bottles:

- 500 mL aliquot for total dissolved inorganic carbon (TDIC) analysis and $\delta^{13}\text{C}$ determination, to which was added specified quantities of SrCl₂ and of KOH (or, in study 1, NaOH) in order to precipitate TDIC as SrCO₃.
- 500 mL aliquot, with no reagents added, for $\delta^{34}\text{S}$ analysis.
- Smaller aliquots (of size 50–100 mL) of groundwater, field filtered at 0.45 μm , for anion and cation analysis.

Soil gas samples

Samples of soil gas in Studies 2 and 3 were collected using a hollow steel probe, inserted at a shallow angle to approximately 10–30 cm depth. A manual pump was used to withdraw soil gas, via a system of valves, to helium-grade balloons. The gas was then circulated between the balloons and bubbled through a flask containing a solution of 25 g SrCl₂ and 0.6 g KOH in 200 ml deionised water (in Study

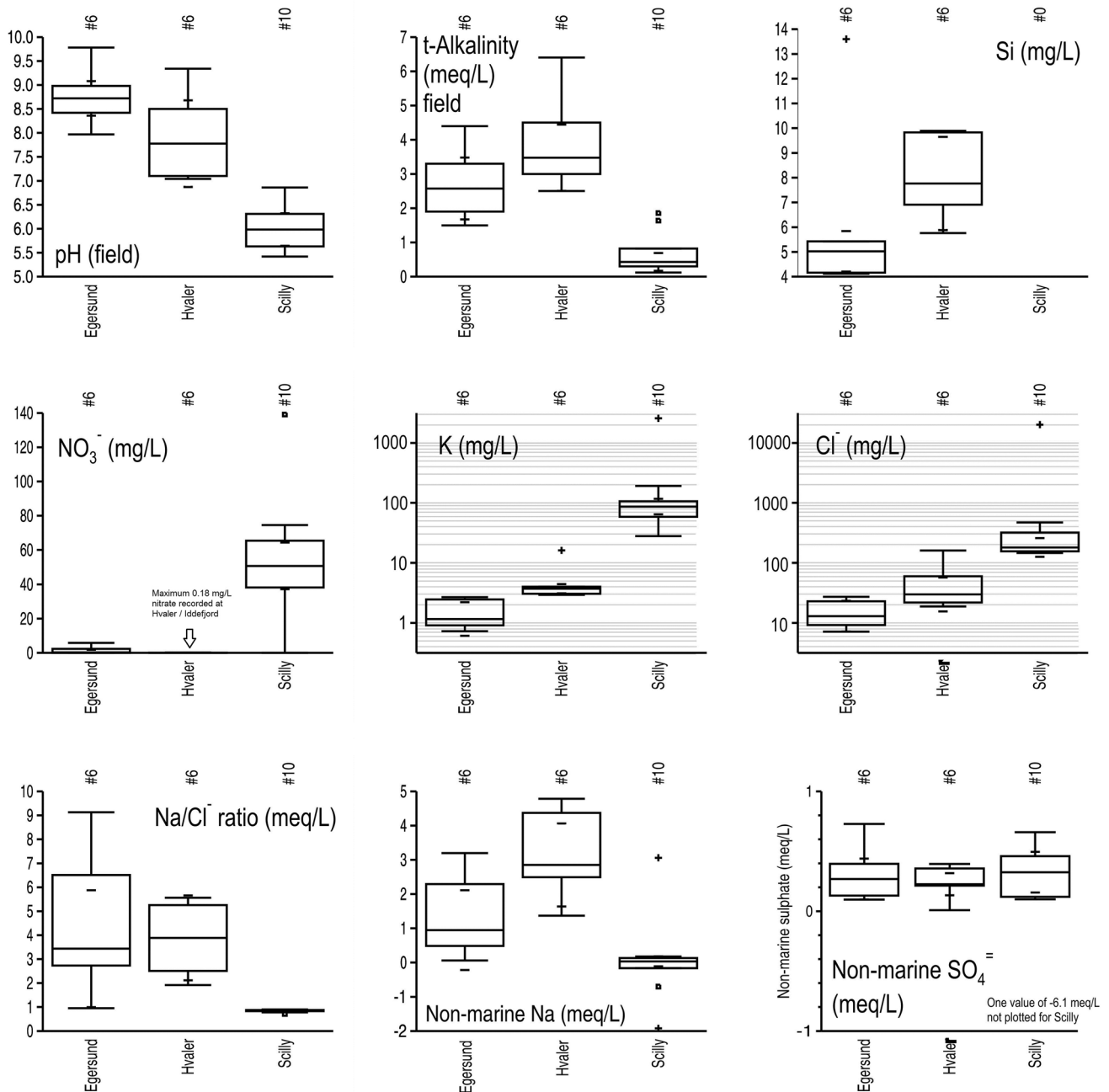


Fig. 3 Boxplots comparing concentrations of various dissolved components in groundwater from the three study areas. In these boxplots, the central box represents the interquartile range (25th–75th percentile), while the central line represents the median, with small horizontal parentheses or “notches” either side the median showing a robust 95% confidence interval on the median. These allow a graphical test of comparability—much like the formal *t* test—of the medians via

notches in the boxplot. The whiskers indicate extraquartile range, with outliers shown as small squares (near outliers) or crosses (far outliers). The # number above each box represents the sample number in the subset. The maximum recorded nitrate concentration in the Hvaler–Iddefjord data set was only 0.18 mg/L—thus, the boxplot is not visible on the selected scale

2, NaOH, rather than KOH was used). This was repeated at least three times. The soil gas CO₂ reacts with the solution and forms a SrCO₃ precipitate. In Study 1, a somewhat less sophisticated method was used, involving transport of soil gas back to the laboratory in the UK in gas-tight vessels.

Studies 1 and 2 were carried out in the summer, and study 3 in the autumn: soil gas CO₂ content (and by implication, its δ¹³C) can vary strongly depending on the temperature and season. The soil gas samples collected can thus, at best, only be regarded as representative of the season of sampling

and not of any annual “average”. Moreover, the soil sampling technique (spike) requires a soil profile of several tens of centimetres depth and will thus have been biased against locations within thinner soils. It should be noted that Study 1 was carried out during a particularly wet episode. This may have inadvertently introduced some sample bias towards well-drained soils (low permeability soils being potentially too waterlogged to permit soil gas sampling). Study 2 was carried out in the same geographical areas, but during a period of particularly fine and dry weather, potentially allowing the sampling of a greater range of soil types, including soils from near wetland areas.

Soil samples

From locations where groundwater or soil gas was sampled, samples of soils were taken (for clarification; the term “soil” refers to organic soils). These were typically taken from 10 to 30 cm depth. In Study 2, samples were subdivided into deep (> 20 cm) and shallow (< 20 cm) samples. Samples were stored and transported in labelled plastic bags.

In addition, from Hvaler (Study 2) a single sample of marine shell sand, encountered in the shallow subsurface profile at one locality, was also sampled.

Vegetation samples

From locations where groundwater or soil gas was sampled, samples of living tissue (leaves or needles) of various common vegetation species in the area were taken. The species were identified. Samples were stored and transported in labelled plastic bags.

Rock samples

Rock samples were typically collected from the outcrops of “freshest” appearance. In Norway, glacial scouring means that many rock outcrops have suffered < 10,000 years sub-aerial weathering. In Scilly, weathering is more intense, so the freshest rock exposures were typically from coastal sections.

Laboratory methodology

For carbon isotope analysis, two types of analytical procedure were typically employed: (1) for inorganic (carbonate) carbon and for (2) organic carbon.

- Groundwater, soil gas, rocks: inorganic carbon

- Plants: organic carbon
- Soils: organic carbon
- Two carbonate-rich soil samples from Scilly: also inorganic carbon
- Marine shell-sand from Hvaler: inorganic carbon

Soil and vegetation samples for organic carbon analysis were treated with H_3PO_4 to remove carbonate carbon and then combusted to release the organic carbon as CO_2 .

For inorganic carbon analysis of groundwater and soil gas samples, inorganic carbon was first immobilized as SrCO_3 precipitate (see “Field methodology” above). Inorganic carbon was typically released from the carbonate by hydrolysis with phosphoric acid (H_3PO_4).

Inorganic carbon isotope analysis

For groundwater samples, the bottles containing the groundwater and SrCO_3 precipitate were weighed and then filtered using a pre-weighed filter and vacuum pump to collect the precipitate, which was thoroughly washed with de-ionized water and dried for 24 h in an oven (~ 110 °C). The dry filter papers were then re-weighed to quantify the dry SrCO_3 precipitate and (once corrected for purity using the manometric analysis of C content during preparation for isotopic analysis—see below) hence groundwater TDIC (total dissolved inorganic carbon). A mass of c. 18–20 mg precipitate was reacted with H_3PO_4 for 10–15 min. For the precipitates from the soil gas samples from Studies 2 and 3, a similar procedure was followed. In Study 1, CO_2 from the gas sample vessels was dried and passed directly into the carbon line (see below).

Rock, soil and shell-sand samples were crushed into a fine powder using an agate grinder, and a quantity of 2.5–3.5 g was weighed out and then reacted with H_3PO_4 for at least 60 min.

The CO_2 released by acid hydrolysis was processed in a purpose-built vacuum line to determine the samples’ carbonate content. The gas was passed through a glass coil immersed in a mixture of dry ice and methylated spirit (~ 80 °C), which removed water vapour by freezing. The residual CO_2 gas was then passed into another part of the line, and the CO_2 content was frozen out by immersion in liquid N_2 (~ -196 °C), and remaining unwanted gases were pumped away. The frozen CO_2 was then allowed to sublime to gas phase in an accurately known volume and the CO_2 pressure (yield) was determined using a capacitance manometer. If the CO_2 yield was high enough, the pure CO_2 gas was passed further down the line where it was again frozen into a valved finger using liquid N_2 . These glass fingers were then sealed, removed and placed into a SIRA mass spectrometer for $\delta^{13}\text{C}$ analysis.

Organic carbon isotope and sulphur isotope analysis

Plant samples were oven-dried and ground using a bladed mill and/or pestle and mortar.

For soil samples, the phosphoric acid/soil mixture resulting from the inorganic carbon extraction (see above) was kept, topped up with deionized water, and left to stand for 24 h, in order for all the inorganic carbon to be released. This was then filtered through a quartz filter paper, dried in an oven for 24 h at ~ 110 °C, and ground to a fine powder.

For $\delta^{34}\text{S}$ analysis of dissolved sulphate in groundwater samples, sufficient 10% HCl solution was added to lower the pH to 2.5–3. Samples were heated to ~ 70 °C and 50 ml of 100 g/L BaCl_2 solution was added to each sample, and left to stand for at least 24 h, until a BaSO_4 precipitate formed. The precipitate was filtered using pre-weighed filter papers and a vacuum pump, washed, dried, and ground to a fine powder.

In both cases, a very small amount of the oven-dried sample powder (~ 0.05 – 1.00 mg for soils/plants and c. 0.2 mg for groundwater precipitate) was placed into tin cups in a tray alongside other standards, and directly inserted into an Isoprime continuous flow mass spectrometer coupled to an Elementar Pyrocube Elemental Analyser, in order to determine organic carbon and sulphur isotope compositions. Organic carbon and sulphur were quantitatively converted to CO_2 and SO_2 by combustion at 1150 °C in the presence of pure oxygen. Water and unwanted gases were scrubbed away before the residual gases were inserted into the mass spectrometer element.

Groundwater chemical analysis

In Study 1, the groundwater samples were returned to the laboratory of the Geological Survey of Norway and analysed for a range of elements by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Perkin Elmer Optima 4300 Dual View instrument and for anions by Dionex DX120 ion chromatography equipment. In Study 3, samples were analysed for major anions and cations using Dionex DX500 and DX600 ion chromatography equipment at the University of Leeds, UK.

Results

Groundwater chemistry: marine influence

All three study localities are in a coastal environment. The groundwater contains dissolved sodium (and, for that matter, also magnesium, sulphate etc.) which may in part be derived from (1) direct intrusion of seawater to the groundwater system, (2) pore waters from marine clays and silts or (3) marine salts in rainfall recharge. These ions can also be

derived from water–mineral interaction (feldspar hydrolysis, carbonate dissolution or sulphide oxidation) and it can often be important to separate out marine-derived sodium (or Mg , SO_4^{2-}) from lithologically derived (or “non-marine”) sodium. This is most conveniently done on the basis of chloride ion concentrations, which are assumed to be wholly derived from marine salts (at least in shallow groundwater systems). Thus:

$$\text{Na}_{\text{nm}} = \text{Na} - \left(\text{Cl} \times \text{Na}_{\text{ocean}} / \text{Cl}_{\text{ocean}} \right) \quad (6)$$

where Na, Cl are the actual sodium and chloride concentrations in groundwater.

Na_{nm} is the non-marine (presumed lithologically derived) sodium concentration.

$\text{Na}_{\text{ocean}}/\text{Cl}_{\text{ocean}}$ is the ratio of concentrations in standard ocean water.

In the case of sulphate, an equivalent calculation is applied, although any “non-marine” sulphate component could be ascribed to lithological sources, or to atmospheric contamination of rainfall recharge by industrial emissions. A “non-marine” sulphate deficit, on the other hand, could be construed as removal of sulphate from the groundwater system, e.g. by sulphate reduction.

Figure 3 shows some key aspects of groundwater chemistry from the three study areas, which corroborate findings from previous studies (Banks et al. 1998—see above). Based on chloride concentrations, the Egersund waters exhibit the least marine influence (typically 10–20 mg/L chloride), then the Hvaler waters (an island group in the Skagerrak, typically 20–60 mg/L chloride). The greatest marine influence is seen in the groundwaters of the Scilly Isles, in the open Atlantic, with typically over 100 mg/L chloride. Indeed, Banks et al. (1997) demonstrate that the highest chloride contents in groundwater are found in the western parts of the Scilly archipelago, facing the prevailing westerly winds. The main source of chloride is believed to be marine salts in rainfall, mist and dry deposition of salts subsequently dissolved in rainfall recharge. Eriksson (1952) notes the relationship proposed by Leeflang (1938) for chloride in Dutch rainfall, namely:

$$\text{Cl (mg/L)} = 3.0 + 11.7 \exp(-0.525 x) + 3.0 \exp(-0.023 x) \quad (7)$$

where x is distance from the coast (km). This implies that, for $x = 1$ km, $\text{Cl}^- = 13$ mg/L and also that marine salt concentrations decrease rapidly within 4 km of the coast. Reviews by Smith (1872) and Eriksson (1952) noted that average chloride concentrations in rainfall along the Scottish coast were 12–13 mg/L, with over 50 mg/L being recorded in North Uist on one occasion, while on the west coast of England, over 50 mg/L was recorded. Banks et al. (1997) recorded 86 mg/L chloride in a rainwater storage tank in Scilly, whilst Banks et al. (1992b) recorded 42 mg/L

chloride in storm runoff from granite terrain in Hvaler. The increasing marine influence on surface water chemistry is demonstrated by Banks et al. (2001), who found clearly increasing concentrations of chloride in surface waters with proximity to the Trøndelag coast of Norway, with > 16 mg/L in the coastal strip.

The nearest rainfall stations monitoring precipitation chemistry are:

- Goonhilly Down, mainland Cornwall, UK, located around 5 km from the coast and 80 km east of Scilly (Conolly et al. 2010; Cape et al. 2014). This station typically exhibits around 10 mg/L chloride in rainfall, but with peaks of over 30 mg/L and higher values during the winter season.
- Birkenes, Norway, located c. 19 km from the coast, some 130 km east of Egersund and 170 km WSW of Hvaler (Aas and Hjellbrekke 2006). This station exhibited on average c. 2–3 mg/L chloride in precipitation in 2006, but with peaks of over 30 mg/L.

Given that it is widely recognised that (a) chloride concentrations in precipitation increase dramatically within 4 km of the coast, (b) salts in rainfall are upconcentrated by several multiples during processes of evapotranspiration on vegetation and in soils (up to three-fold in Wales; Neal and Kirchner 2000), and (c) they are augmented by dissolution of dry salt fallout; the chloride concentrations observed in Fig. 3 are believed to be consistent with marine derivation.

In Fig. 3, it should be noted that the Scilly waters exhibit an Na/Cl ratio similar to sea water and generally negligible

non-marine sodium (i.e. little evidence of feldspar weathering). The Scilly waters are all of Na-Cl type. It should be noted that one of the Scilly samples was from a coastal borehole specifically abstracting saline groundwater for desalination. The groundwater is thus effectively infiltrated ocean water ($\text{Cl}^- = \text{c. } 20 \text{ g/L}$, $\text{Na} = 11 \text{ g/L}$). The Norwegian waters, on the other hand, exhibit an $\text{Na/Cl} > 1$ and significant non-marine (presumed lithological) sodium.

Groundwater chemistry: other (non-marine) aspects

The Norwegian waters typically had a circum-neutral or (especially in Egersund area) somewhat alkaline pH and a moderate alkalinity in the range 1.5 to 6.4 meq/L. The Scilly waters were considerably less hydrochemically mature, with pH values mostly < 6.5 and alkalinities mostly < 1 meq/L. Scilly groundwaters were also characterised by elevated chloride (location in open Atlantic), generally elevated nitrate (median 51 mg/L as NO_3^-) and potassium (several tens to over 100 mg/L, presumed to be related to leaching from agriculture).

The Norwegian waters were characterised by rather modest calcium concentrations (< 30 mg/L; Fig. 4), low calcium/alkalinity meq ratios (less than unity), very high Na/Ca ratios and high non-marine sodium concentrations. Of the Norwegian waters, those from Hvaler–Iddefjord typically exhibited the higher alkalinities, silicon concentrations and non-marine sodium excesses, indicating a greater degree of hydrochemical maturity and silicate hydrolysis. The Hvaler–Iddefjord waters are all of Na- HCO_3 type (or, in one case, Na-Cl- HCO_3), while the Egersund waters are either Na- HCO_3 or Mg-(Ca-Na)- HCO_3 type.

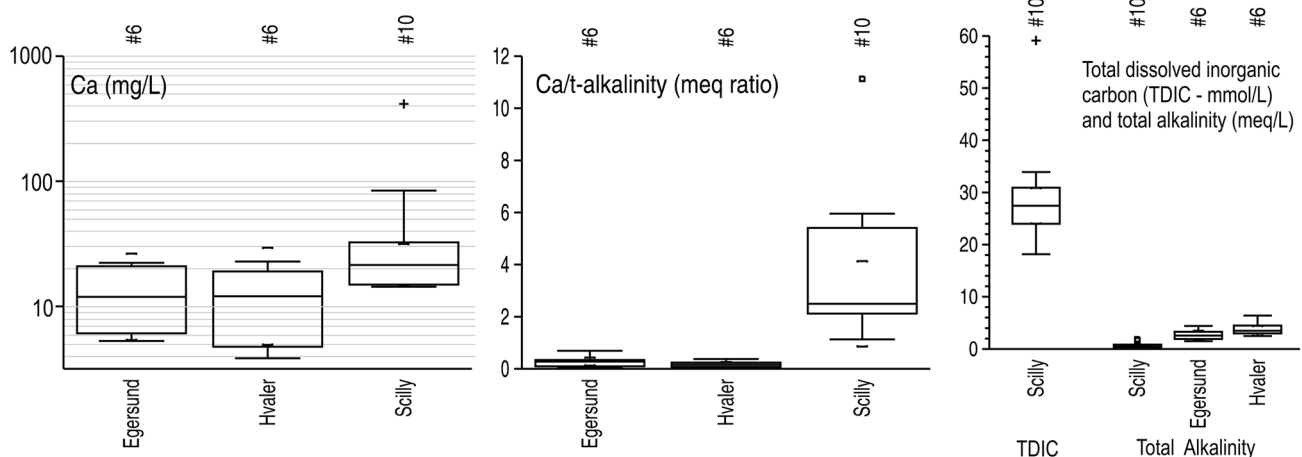


Fig. 4 Boxplots comparing (left) concentrations of calcium in groundwater from the three study areas; (centre) the calcium/alkalinity ratio in meq/L and (right) the TDIC and total alkalinity (t-alkalinity) contents of the groundwaters (the single high TDIC value of

59 mmol/L is from the coastal saline borehole discussed in the text). The high calcium/alkalinity ratios at Scilly are partly ascribable to the strong influence of marine salts on the groundwater (sea water has a Ca/alkalinity meq ratio of c. 8.6—Dickson and Goyet 1994)

There was little evidence of significant depletion in sulphate due to sulphate reduction (Fig. 3)—indeed a slight non-marine sulphate excess was observed in most samples (with a median non-marine sulphate concentration of 0.2–0.3 meq/L in all three study areas), potentially ascribable to industrial sulphur oxide dissolution in recharge water, or to oxidative dissolution of geological sulphide minerals. The degree of marine influence can be seen in Fig. 5, where the groundwater sulphate $\delta^{34}\text{S}$ signature is plotted against the sulphate/chloride meq ratio. The marine-influenced (e.g. Scilly) waters plot to the top left, close to standard ocean water. Where excess sulphate is present, the $\delta^{34}\text{S}$ decreases to values around 0‰ in Egersund and to negative values in Hvaler–Iddefjord Granite. This decrease reflects an increased component of non-marine sulphate, e.g. industrial sulphur dioxide entrained in rainfall recharge or from oxidation of bedrock sulphides (Krouse and Mayer 2000; Taylor et al. 1984). Only one sample exhibits a sulphate deficit (relative to sea-water ionic ratios) of 6.1 meq/L—namely, the highly saline borehole on Scilly (infiltrating marine water)—possibly indicating a modest degree of sulphate reduction.

From the known pH-dependent chemistry of the carbonate system (Mook 2000), it is reasonable to assume that, at $\text{pH} > 7$ (Norwegian groundwater samples) the CO_2 dissolved in recharge water has reacted with basic mineral phases and that the total dissolved inorganic carbon (TDIC) is largely in the form of HCO_3^- (alkalinity). For the Scilly samples, with their low pH values, this is not the case and TDIC was independently determined on the Scilly groundwaters. In fact, typical TDICs of 18–34 mmol/L were found (Fig. 4)—implying that most of the inorganic carbon found in the Scilly groundwaters is still in the form of unreacted carbonic acid ($\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3$) and very little

(typically < 1 mmol/L) has reacted with mineral phases to form HCO_3^- . The ratios of TDIC to alkalinity approximately correspond with those theoretically predicted at pH values of around 5.5 (Mook 2000).

Vegetation, soils and soil gas

The three study areas all show very similar ^{13}C signatures in vegetation, irrespective of species sampled: the bulk of the determinations are in the range $\delta^{13}\text{C} = -27$ to -30 ‰ (Fig. 6).

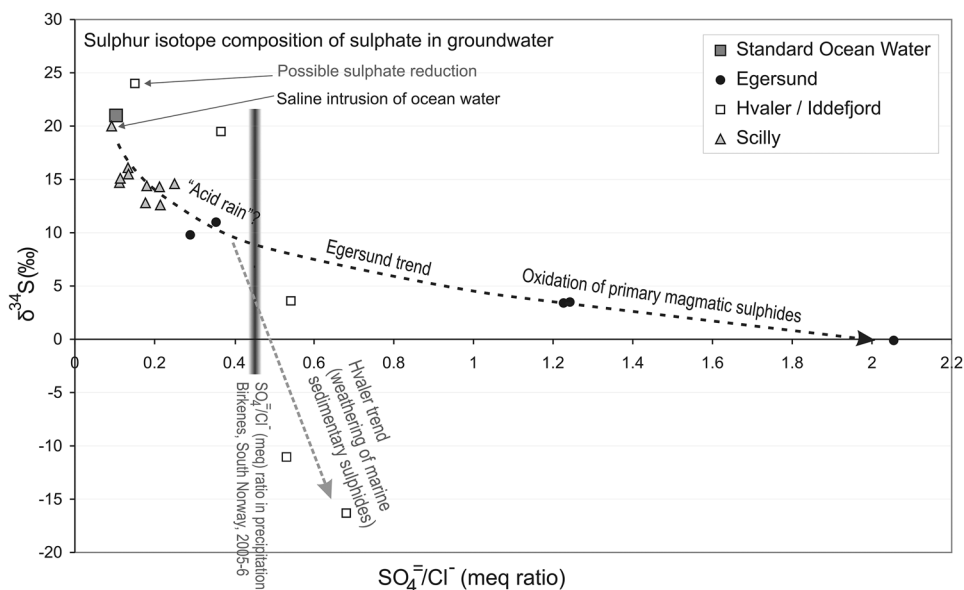
The $\delta^{13}\text{C}$ signatures of the organic component of the soils (-30 to -26 ‰) fall within the same interval as the vegetation samples (Fig. 6).

The carbonate content of soils was determined only on samples from Scilly and contents ranging from < 0.001 to 0.01% were found, with one sample of beach soil containing just over 0.4% (Fig. 7). Carbon isotope analysis was possible of two samples of inorganic soil carbonate (the high-carbonate Scilly beach soil, and a sample of pedogenic carbonate extracted from another Scilly soil sample), returning $\delta^{13}\text{C}$ signatures of $+2.1$ and -15.2 ‰ respectively (Fig. 6).

The marine shell sand occurring in the shallow subsurface at one location in Hvaler returned a marine inorganic carbonate signature close to zero.

Significant differences arise between the $\delta^{13}\text{C}$ analyses of soil gas, however, with the soils of Scilly returning the lightest signatures, typically in the range -30 to -26 ‰; i.e. very similar to soils. The soil gas samples from Egersund are the heaviest, typically in the range -17 to -12 ‰ (for both Studies 1 and 2). The soil gas samples

Fig. 5 Groundwater sulphate $\delta^{34}\text{S}$, plotted against $\text{SO}_4^{2-}/\text{Cl}^-$ meq ratio for the sampled groundwaters. Typical ocean water has $\delta^{34}\text{S} = c. 21$ ‰ (Mayer 2007; Rees et al. 1978) and $\text{SO}_4^{2-}/\text{Cl}^-$ meq ratio = 0.103 (Dickson and Goyet 1994). Precipitation at Birkenes, southern Norway, has a typical $\text{SO}_4^{2-}/\text{Cl}^-$ meq ratio around 0.45 in 2005/2006 (Aas et al. 2006, 2007), while anthropogenic sulphate in the precipitation of the northern hemisphere usually ranges from -3 to $+9$ ‰ (Krouse and Mayer 2000)



from Hvaler–Iddefjord exhibit a large range, intermediate between Scilly and Egersund.

Rock

Samples of anorthosite/granite bedrock were taken from all three study areas. Samples were of surface outcrops, which (because of the subaerial weathering histories) would be expected to be “fresher” and less weathered in Norway than in the Scilly Isles. Contents of carbonate were typically in the range < 0.001 to 0.02%, with somewhat higher contents being found in the Egersund area than in the Isles of Scilly (in line with expectations from the hypotheses of Banks et al. 1997, 1998). A few Norwegian samples exhibited higher carbonate contents in the range 0.07–0.12% (Fig. 7).

$\delta^{13}\text{C}$ compositions of bedrock carbonates were in the range -13 to -3‰ in the Norwegian samples, with heavier compositions recorded from the Scilly granites, in the range $+0.1$ to -1.9‰ (Fig. 6).

Groundwater

The $\delta^{13}\text{C}$ determinations of the TDIC in the bedrock groundwater also exhibit significant differences between the three areas. In this context, it should be remembered that:

- in the Norwegian (high pH) samples, the TDIC is primarily composed of HCO_3^- and (in the highest pH samples) CO_3^{2-} . In other words, assuming a closed system with respect to CO_2 , the CO_2 in the recharge water has almost completely reacted with basic mineral phases.
- in the lower pH Scilly groundwaters, the TDIC is primarily composed of unreacted ($\text{CO}_2 + \text{H}_2\text{CO}_3$), with only a modest portion having reacted to form HCO_3^- .

The Egersund groundwaters predominantly exhibit heavy $\delta^{13}\text{C}$ signatures in the range -14 to -20‰ (Fig. 6), while those from Hvaler–Iddefjord Granite are not dissimilar, clustering around -18‰ . The Scilly groundwaters, on the other hand, exhibit groundwater $\delta^{13}\text{C}$ signatures of -22 to -26‰ . A single groundwater sample from Scilly returned a $\delta^{13}\text{C}$ of -4.9‰ : this was from the coastal borehole specifically abstracting saline groundwater for desalination. The groundwater is thus largely effectively infiltrated ocean water ($\text{Cl}^- = c. 20 \text{ g/L}$) and is thus heavily influenced by the marine $\delta^{13}\text{C}$ (nominally 0‰).

Discussion

The vegetation and soil $\delta^{13}\text{C}$ signatures are unsurprising. The soil gas signatures do, however, show significant differences, both from each other and from their parent soils.

The Scilly soil gas has a very similar signature to its parent soils, suggesting either a high soil CO_2 production rate, or a low rate of soil diffusion (low permeability, deep samples) or both. All the Egersund soil gas samples from Studies 1 and 2 (Fig. 8) have a $\delta^{13}\text{C}$ signature significantly heavier than the soil's organic carbon $\delta^{13}\text{C}$ (and much greater than the “ideal” $+4.4\text{‰}$ relative fractionation suggested by Cerling et al. 1991, see above). The “heavy” Egersund soil gas signature could potentially be related to a low soil CO_2 production rate or to the fact that the Egersund soil profiles and superficial cover tend to be rather thin, leading to enhanced diffusion of light ^{12}C and/or mixing with atmospheric CO_2 . The Hvaler–Iddefjord granite soil gas samples range from having a similar signature to the soils to significantly heavier. The results for Hvaler–Iddefjord are study-dependent, those from Study 1 being significantly heavier than those from Study 2 (Fig. 8), possibly reflecting the different methodologies being used (though no effect was seen in the Egersund sampling). This effect could be related to the possibility that, because of generally wet conditions during Study 1, well-drained, higher permeability soils were preferentially sampled—i.e. soils permitting diffusive loss of ^{12}C . Study 2 was dry enough to permit the sampling of at least one soil from near a wetland area, returning the isotopically lightest soil gas sample from Hvaler–Iddefjord; one may speculate whether there may here have been a contribution from oxidation of isotopically light methane.

With regard to the granite/anorthosite rocks, the observed wide range in rock carbonate content and isotopic signature is perhaps unsurprising, given the differences in weathering history, the difficulties in representative sampling and the wide variety of potential mechanisms for genesis of calcite within the rock matrix or along fractures of different generations. Future studies should aim to obtain a more representative host rock data set.

To interpret the groundwaters, the ^{13}C isotopic signatures of the TDIC content have been plotted in Fig. 9, firstly against pH and secondly against alkalinity. These diagrams also show the theoretical idealised evolutionary trajectories of a closed silicate weathering system (vertical arrows in both cases, where the soil gas signature is essentially preserved in the groundwater TDIC), a closed carbonate weathering system and an open system (irrespective of whether it is silicate or carbonate weathering), for each of three soil gas compositions: -26‰ , -21‰ and -16‰ (resulting in dissolved CO_2 isotopic signatures of -27.1 , -22.1 and -17.1‰ , due to the -1.1‰ fractionation on dissolution of CO_2 gas—Table 2). In the case of the alkalinity plot, the evolution also depends on the initial soil gas PCO_2 : the diagram shows curves for $10^{-1.5}$ atm (the maximum value observed by Banks and Frengstad 2006), $10^{-2.0}$ and $10^{-2.5}$ atm.

The Scilly groundwater TDIC shows a very light $\delta^{13}\text{C}$ signature, similar to both soil and soil gas. This is entirely

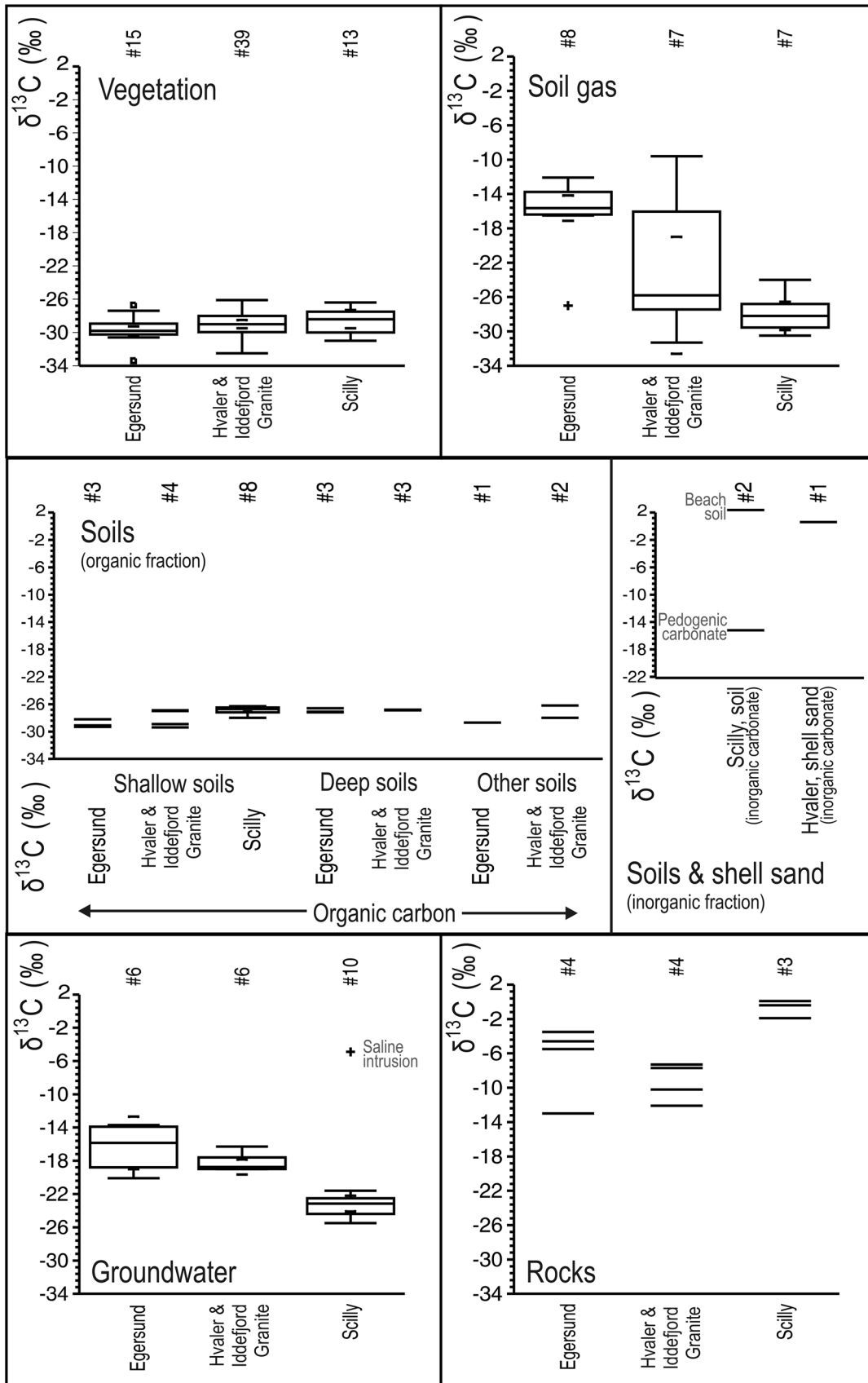


Fig. 6 Boxplots comparing $\delta^{13}\text{C}$ signatures in the three study areas for six different environmental media (vegetation, soils—organic fraction, soils and shell sand—inorganic fraction, soil gas, rocks and groundwater). # = sample number for each subset

consistent with the expectation that the TDIC largely comprises dissolved CO_2 in these low pH waters, only a small fraction having reacted with basic aquifer minerals to raise pH and release bicarbonate alkalinity. The results (Fig. 9) are all consistent with either open system carbonate or silicate weathering, with a soil gas $\delta^{13}\text{C}$ of -26‰ , or closed silicate weathering with a slightly lower initial soil gas $\delta^{13}\text{C}$ of -21 to -25‰ . Given that the actual soil gas determinations were typically -26 to -30‰ , the former is the more likely. Thus, although the results are entirely self-consistent, they do not allow us to distinguish between Models A (carbonate) and B (silicate weathering). One outlying point is seen on both diagrams in Fig. 9—the highly saline groundwater from Scilly, which is essentially intruding ocean water and whose $\delta^{13}\text{C}$ signature is strongly influenced by the marine value.

The Hvaler–Iddefjord granite groundwater $\delta^{13}\text{C}$ signatures are all very similar at around -17 to -19‰ . While vegetation/soil signatures were typically -30 to -27‰ , there was a wide spread of $\delta^{13}\text{C}$ in the soil gas determinations themselves, ranging from similar to the soil to similar to the groundwater. In Fig. 9, the alkalinity results all fall within the “open CO_2 ” weathering field, consistent with a soil gas of $\delta^{13}\text{C} = c. -26\text{‰}$, and $\text{PCO}_2 = 10^{-2}$ to $10^{-1.5}$ atm. On the other hand, the results would be equally consistent with a closed silicate weathering system, commencing with a soil gas composition of -16 to -19‰ (which is still consistent with the field soil gas results). The pH results plot close to, but mostly slightly to the left of the -26‰ “open CO_2 weathering” curve, implying either a somewhat isotopically lighter soil gas, or a component of closed silicate weathering. More significantly, the high pH values would be difficult to explain within an open CO_2 evolutionary pathway, where the presence of a permanent reservoir of CO_2 would keep pH values depressed (Fig. 10). On balance, therefore, the Hvaler–Iddefjord results suggest that some degree of closed system silicate weathering (Model B) has been important—at least during the later stages of evolution of the higher pH waters.

In Egersund, both Studies 1 and 2 result in a relatively narrow range of soil gas $\delta^{13}\text{C}$ determinations of around -14 to -16‰ —somewhat heavier than might have been expected. Groundwater TDIC exhibits a generally similar (though broader) signature (-14 to -20‰). Taken at face value, this similarity is consistent with a closed system silicate hydrolysis (Model B) evolutionary pathway. In Fig. 9 (top), the theoretical dependences of TDIC $\delta^{13}\text{C}$ on pH for closed silicate (arrows), closed carbonate (dashed lines) and open carbonate or silicate systems are shown for

aquifer carbonate $\delta^{13}\text{C}$ of 0‰ and soil gas ($\text{CO}_{2(\text{gas})}$) $\delta^{13}\text{C}$ of -26‰ , -21‰ and -16‰ . The pH values at which calcite saturation is achieved for $\text{PCO}_2 = 10^{-2.5}$ to $10^{-1.5}$ atm. are shown as shaded zones for closed (pH c. 7.6–9.1) and open (pH c. 7–7.6) carbonate systems, respectively. Figure 9 (lower part), the theoretical dependences of TDIC $\delta^{13}\text{C}$ on pH for closed silicate (vertical arrows), closed carbonate (lower triangular fields) and open carbonate or silicate systems (tall triangular field) are shown for aquifer carbonate $\delta^{13}\text{C}$ of 0‰ and soil gas $\delta^{13}\text{C}$ of -26‰ , -21‰ and -16‰ . Within each open system and closed carbonate system field, three evolutionary lines are shown, corresponding with $\text{pCO}_2 = 10^{-2.5}$, 10^{-2} and $10^{-1.5}$ atm. In Fig. 9, some of the Egersund samples fall on open system evolutionary trajectories, starting with soil gas CO_2 $\delta^{13}\text{C}$ in the range -21 to -26‰ , while two others (at least on the pH diagram) fall to the left of the marked curves, suggesting even lighter soil gas CO_2 $\delta^{13}\text{C}$. Such values are incompatible with the soil gas determinations recorded in the field studies. As with the Hvaler–Iddefjord samples, the high pH values of some of the samples would also appear incompatible with a wholly “open CO_2 ” weathering pathway (Fig. 10).

On balance, therefore, the combination of pH, alkalinity and TDIC $\delta^{13}\text{C}$ groundwater analyses is strongly suggestive that silicate weathering, partially in a system closed with respect to CO_2 , is important in the evolution of Norwegian bedrock groundwater chemistry, as well as open weathering pathways. However, $\delta^{13}\text{C}$ results have not proven to be, at least in this study, an unambiguous tool for distinguishing between carbonate and silicate weathering, largely because the ideal “open CO_2 ” pathways for these are essentially identical. Moreover, Banks and Frengstad (2006) point out, in their study of groundwater chemical evolution in the Egersund anorthosites, that these hypothetical pure open or closed silicate or carbonate weathering pathways are too simplistic. Real groundwater evolutionary pathways are likely to include hybrid (and intermediate) mechanisms: for example, they argue that some degree of openness (with respect to CO_2) is necessary to evolve the rather high alkalinities and dissolved solute concentrations observed in many Norwegian samples, while some degree of closure is required to generate the relatively high pH values of some samples (Fig. 10).

One of the issues revealed in this study has been the observation, in the case of the Norwegian sites, that the soil gas is often significantly isotopically heavier than the parent soil materials. The low sample density and lack of depth variation and seasonal variation in soil gas sampling was a major hindrance to interpreting results. There also remains the potentially awkward question of whether the soil gas extraction method employed adequately represents the soil gas that dissolves in recharging groundwater to form carbonic acid—i.e. the main source of acidity for

Fig. 7 Boxplots comparing soil and rock carbonate contents in the three study areas

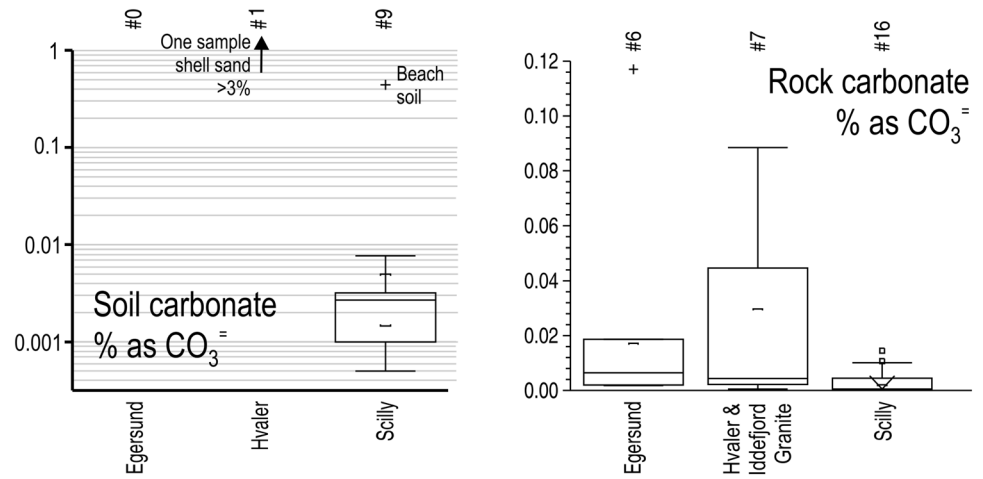


Fig. 8 Boxplots illustrating the evolution of $\delta^{13}\text{C}$ signatures between different media in the three different study areas. For clarification, the four left-hand columns (vegetation, shallow, deep and other soil) all refer to analyses of the organic carbon fraction. The data from the Scilly Isles are all from Study 3

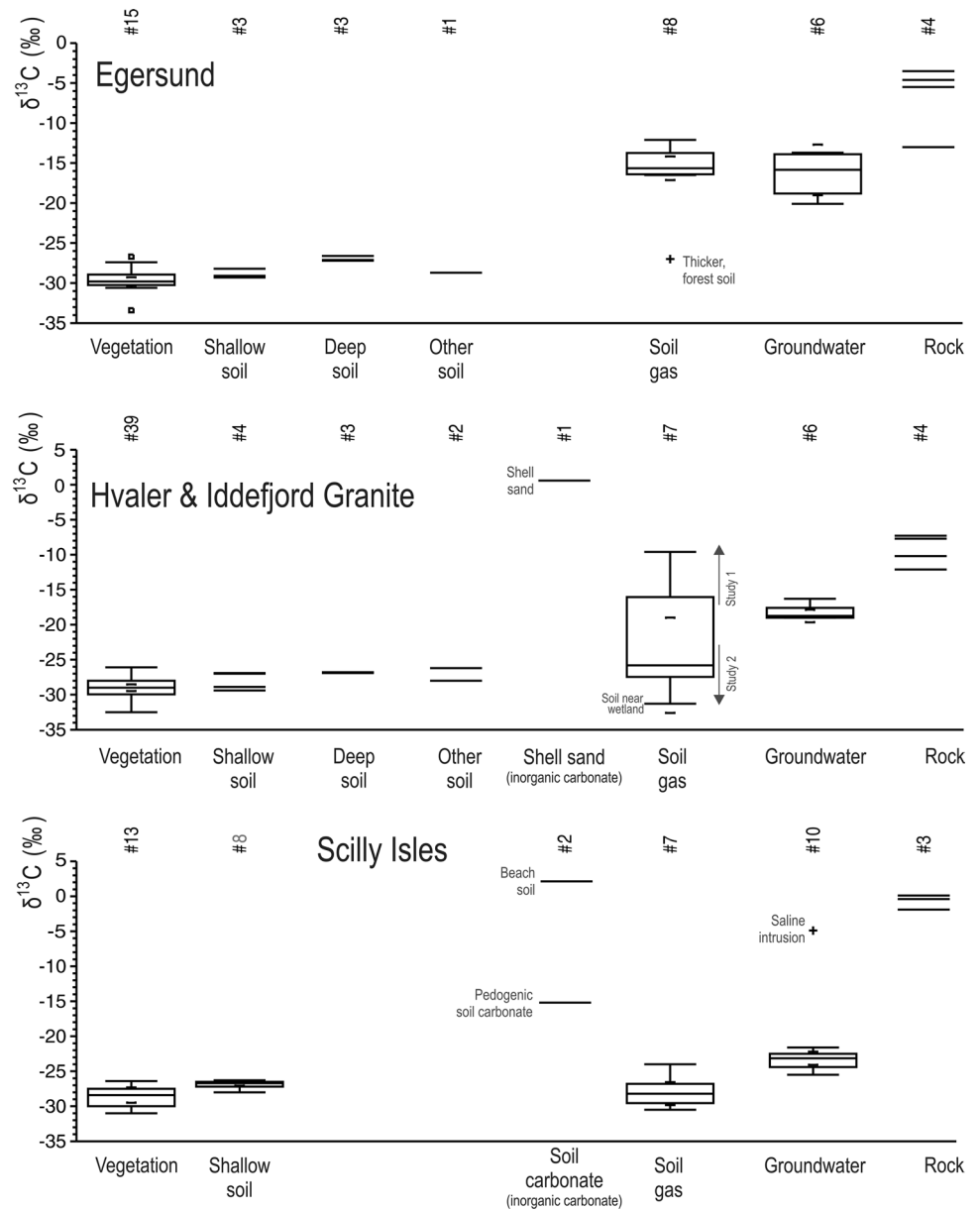
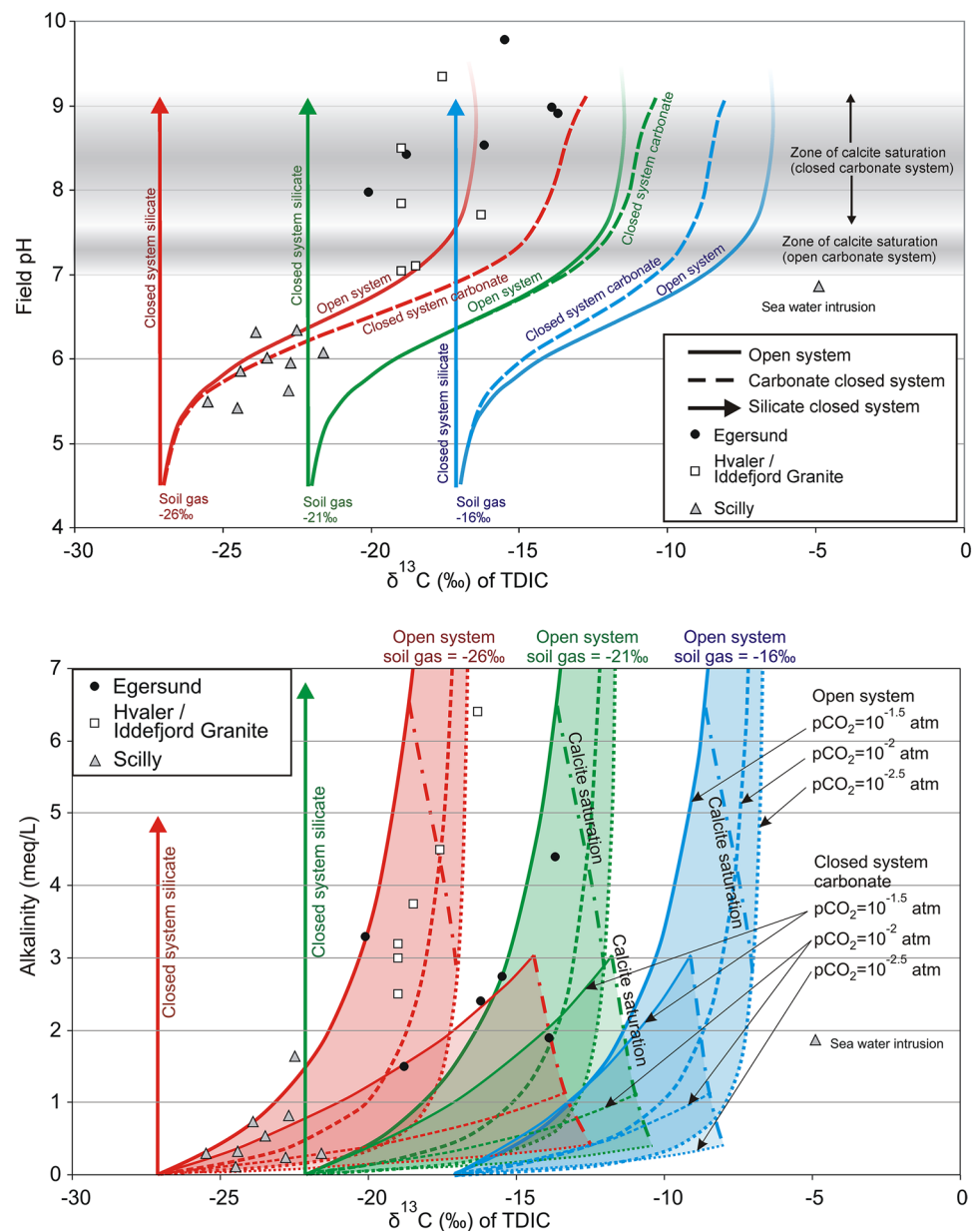


Fig. 9 Plot of (top) field pH and (bottom) field alkalinity against groundwater TDIC $\delta^{13}\text{C}$ signatures for the three study areas. Theoretical dependences of TDIC $\delta^{13}\text{C}$ on (top) pH and (bottom) alkalinity for closed silicate (arrows), closed carbonate and open carbonate or silicate systems are shown for various soil gas $\delta^{13}\text{C}$ and an aquifer carbonate $\delta^{13}\text{C}$ of 0‰. Chemical speciation is calculated at 10 °C using the model PHREEQC Interactive (Parkhurst and Appelo 1999), while isotopic composition is calculated using the methodology of Deines et al. (1974) and the fractionation constants provided by Clark and Fritz (1997, Table 2). See text for further explanation



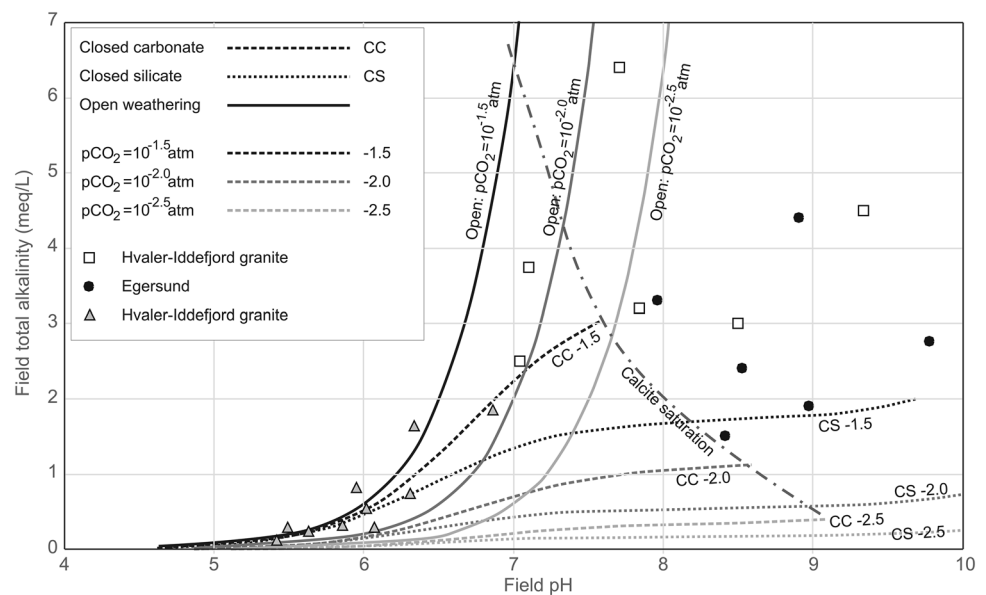
carbonate and silicate hydrolysis. The sampling method employed in these studies (suction via a steel tube) may favour high permeability and porosity volumes of the soil, whereas intimate soil gas–water–rock interaction may favour small pore spaces with low permeability and high surface area. Samples of soil gas in Norway were taken in the summer, yet much of the recharge occurs in the autumn through to spring snow-melt (at least in low-lying areas where ground is not frozen in the winter), when the soil CO_2 concentrations and $\delta^{13}\text{C}$ may be significantly

different. Future studies should focus on more representative and rigorous $\delta^{13}\text{C}$ sampling of soil gas and of unsaturated zone soil water (recharge water), both in space and time, to better constrain the results.

Conclusion

Banks and Frengstad (2006) pointed out that many of the hydrochemical evolutionary features of crystalline bedrock

Fig. 10 Field-derived pH and alkalinity data from the three study areas, plotted on theoretical evolutionary trajectories (calculated using PHREEQC at 10 °C—Parkhurst and Appelo 1999) for open CO₂ weathering, closed silicate weathering and closed calcium carbonate weathering systems. The calcite saturation curve only applies to the calcium carbonate weathering trajectories; for silicates, the point of calcite saturation will depend on the cationic composition of the silicates and the solution



groundwater can be explained by hydrolysis of aluminosilicate mineral phases (so-called Model B—equations 2, 3). They contrasted this with an alternative model whereby alkalinity and base cations are generated by kinetically rapid hydrolysis of carbonate minerals in superficial deposits or along fracture surfaces, followed by ion exchange to increase sodium concentrations, deplete calcium and allow further accumulation of alkalinity, resulting in an alkaline sodium bicarbonate water type (so-called Model A—equations 1a, 1b). Several authors, including Banks and Frengstad (2006) and Schulte et al. (2011), also hypothesised that an examination of ¹³C in groundwater TDIC may be able to distinguish between the two models.

This question is of interest for pure academic reasons—rather few studies have questioned the ultimate source of TDIC in groundwater in crystalline bedrock aquifers or have characterised ¹³C signatures in their groundwaters. It also has a practical interest—consumption of CO₂ by mineral hydrolysis is a significant global CO₂ sink (Brady 1991; Liu and Zhao 2000; Probst et al. 1998; Gaillardet et al. 1999; Amiotte-Suchet et al. 2003; Beaulieu et al. 2012) and large areas of the globe are underlain by crystalline rock terrain. The predominance of Model A in generating groundwater alkalinity potentially may lead to no permanent net CO₂ sink, as CO₂ can ultimately be re-released (Eq. 4) to the atmosphere. Model B potentially represents a 50% net sink for CO₂.

This study has examined the evolution of the ¹³C signature from vegetation, through soil, soil gas and rock carbonate, to groundwater TDIC at several discrete localities within two Norwegian and one British crystalline rock terrains. In the first study area, the granitic Scilly Isles of south-west England, the groundwaters were very immature

hydrochemically and most of the groundwater TDIC was in the form of carbonic acid, reflecting the soil gas ¹³C isotopic signature.

In the Iddefjord Granite study area of south-east Norway, a wide range of soil gas δ¹³C was found. However, groundwaters typically exhibited δ¹³C of around −18‰, irrespective of alkalinity. The groundwater δ¹³C signature could be construed as compatible with either closed system (with respect to CO₂) silicate weathering or open system silicate or carbonate weathering. The combination of high pH and light δ¹³C in some samples does, however, suggest at least a component of closed system silicate weathering.

In the Egersund study area of south-west Norway, the soil gases were unexpectedly isotopically heavy, typically ranging from −12 to −17‰. Groundwaters also exhibited a range of −14 to −20‰, which similarity also tentatively offers support for at least a component of closed system silicate weathering.

The three studies reported in this paper have demonstrated that:

- δ¹³C analyses are not a simple technique to distinguish between silicate and carbonate weathering pathways, partially because ideally “open” (with respect to CO₂) evolutionary trajectories are essentially identical for silicate and carbonate weathering.
- The notion of a clear distinction between “closed” and “open” (with respect to CO₂) and between carbonate and silicate weathering pathways is conceptually flawed. Accumulating evidence from Norwegian crystalline bedrock aquifers strongly suggests that hybrid or intermediate pathways are more likely (and arguably necessary to

explain some combinations of features, such as both high pH and high alkalinity).

To achieve a better understanding of ^{13}C isotope systematics in crystalline bedrock environments, more attention needs to be given to the characterisation of (1) the soil gas system's behaviour and isotopic signature throughout the seasons, (2) how carbon dioxide is solubilised and reacts in the early stages of groundwater evolution and (3) whether, and at what stage, the weathering system becomes closed with respect to CO_2 . In particular, in future studies:

1. A limited number of study sites in Norway should be prioritised and greater effort expended in sampling soil gas at different depths and seasons throughout the soil profile/unsaturated zone, preferably on a three-dimensional grid at each sampling locality.
2. Following soil-gas sampling, the soil profile should be excavated and the mineralogy and grain-size distribution characterised with depth.
3. Lysimeters should be installed in the unsaturated zone and/or at the drift/bedrock interface, such that recharging water can be sampled for alkalinity, pH, isotopic signature and groundwater chemistry, in order to better constrain the isotopic signature evolution between soil gas and downward percolating recharge.

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