Carbon dioxide drawdown by Devonian lavas

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ABSTRACT: Lower Devonian volcanic rocks in the northern British Isles, especially Scotland, show extensive evidence for contemporaneous subaerial weathering. Basalt and andesite lavas were altered to red iron oxides, commonly accompanied by calcite. Measurement of carbonate contents in 104 samples over a region of 100,000 km^2 show an average of 13% calcite. Weighted for outcrop thickness, this represents an estimated 7.3×10^{16} moles CO_2, extracted from surface waters and ultimately the atmosphere. The time frame for this drawdown is difficult to constrain, but complete weathering of a one-metre unit over 1000 years would involve CO_2 consumption comparable with the highest rates determined in modern basaltic watersheds. These data demonstrate that volcanic activity can be a major sink, as well as a source for CO_2, and provide a data set for modelling of CO_2 flux during episodes of volcanic activity in the geological record. The high capacity of the Devonian lavas for CO_2 drawdown emphasises the potential of basalts for CO_2 sequestration.

KEY WORDS: Basalt, CO_2 sequestration, Old Red Sandstone, Scotland

In the quest to find suitable rocks that may be used to sequester carbon dioxide (CO_2) from natural and/or industrial sources, basalts have emerged as particularly prospective (Schaef *et al.* 2010). The alteration of basalts, including carbonation, takes place relatively readily, and basalt weathering has been studied in detail (Dessert *et al.* 2003; McGrail *et al.* 2006; Oelkers *et al.* 2008). Accordingly, basalts may have the potential to sequester CO_2 in mineral form rather than simply acting as storage sites for CO_2. Advanced initiatives are investigating specific sites in volcanic rocks for CO_2 sequestration, including in Iceland (Alfredsson *et al.* 2008; Gislason *et al.* 2010), the Deccan basalts, India (Prasad *et al.* 2009), the Newark Basin, USA (Matter *et al.* 2007) and the Columbia River basalts, USA (Schaef & McGrail 2009; Tollefson 2013). This strategy assumes sequestration by reaction of CO_2 with primary basalt minerals to yield carbonates (especially the magnesium carbonate mineral magnesite). The age of the basalts targeted for sequestration is not a consideration, including rocks about 200 million years old in the Newark Basin (Matter *et al.* 2007).

An alternative perspective considers the role of volcanic rocks in the CO_2 budget during and immediately after eruption. CO_2 is an important component of volcanic degassing, and models for atmospheric evolution assume that periods of volcanic activity cause an increase in atmospheric CO_2 (Frakes *et al.* 1992). However, there is also potential for freshly erupted volcanic rock to undergo weathering and thereby consume CO_2 (Varekamp & Thomas 1998; Dessert *et al.* 2003; Berner 2006). This fresh new crust is rich in minerals which are relatively unstable at the Earth's surface, and can be altered at a fast rate. The chemical weathering of basalts occur 5–10 times faster than the weathering of granites and gneisses (Dessert *et al.* 2001). This is especially likely in warm tropical climates, which experience the most intense chemical weathering. As a general rule, bicarbonate concentrations in run-off water, and hence CO_2 consumption by weathering, increase with temperature (Dessert *et al.* 2003). Thus, basalts in a hot climate have the potential for substantial CO_2 drawdown.

Quantitative estimates of CO_2 sequestration that might be possible in large basaltic provinces today have been determined (Dessert *et al.* 2003). However, there are no measurements of natural drawdown into basalts from the geological record for comparison. The optimum combination for drawdown, of voluminous continental volcanic activity and warm climate, was in the Devonian period (Frakes *et al.* 1992) when the atmosphere was CO_2-rich (Berner 2006).

1. Lower Devonian lavas in the British Isles

This study reports data from Lower Devonian volcanic rocks in the northern British Isles. Several outcrops of basaltic and andesitic lavas occur in Scotland, northern England, Northern Ireland, and the Republic of Ireland (Fig. 1). The lavas were deposited in a terrestrial environment, inter-bedded with sandstones and conglomerates in successions of 'Old Red Sandstone'. The conglomerate beds contain abundant clasts of the lavas. The outcrops were probably once part of a continuous expanse of subaerial volcanic rocks that extended across the major lineaments of the Highland Boundary Fault and Southern Uplands Fault (Trench & Haughton 1990; Browne *et al.* 2002), and occupied at least 100,000 sq. km (Fig. 1). Their cumulative thickness varies from <100 m up to 2.5 km in central Scotland. The volcanic activity has been related to subduction on the northwest margin of the Iapetus Ocean (Thirlwall 1988). The lavas in this setting are typically andesitic, and in such lavas the primary volatile component has a high H_2O/CO_2 ratio. The palaeolatitude of northern Britain in the lower Devonian was near-equatorial, and the climate was tropical: Lower Devonian temperatures were in the range of 30–35°C (Joachimski *et al.* 2009).

The dating of the lavas is possible through radiometric dating of the lavas themselves, and through spore zonation of accompanying terrestrial sedimentary rocks. In some cases, a specific Lower Devonian stage can be determined (Fig. 2), but in the Curlew Mountains (Graham & Clayton 1988) and the St. Abbs and Cheviots (Stephenson 1999) regions, only a broad Lower Devonian age can be attributed. The spore-defined ages are mostly in the Lochkovian–Pragian stages (Fig. 2). Where lavas are dated radiometrically, the dates obtained are broadly consistent with the palynological ages. In Fife/Angus, dating was possible by both methods, and is
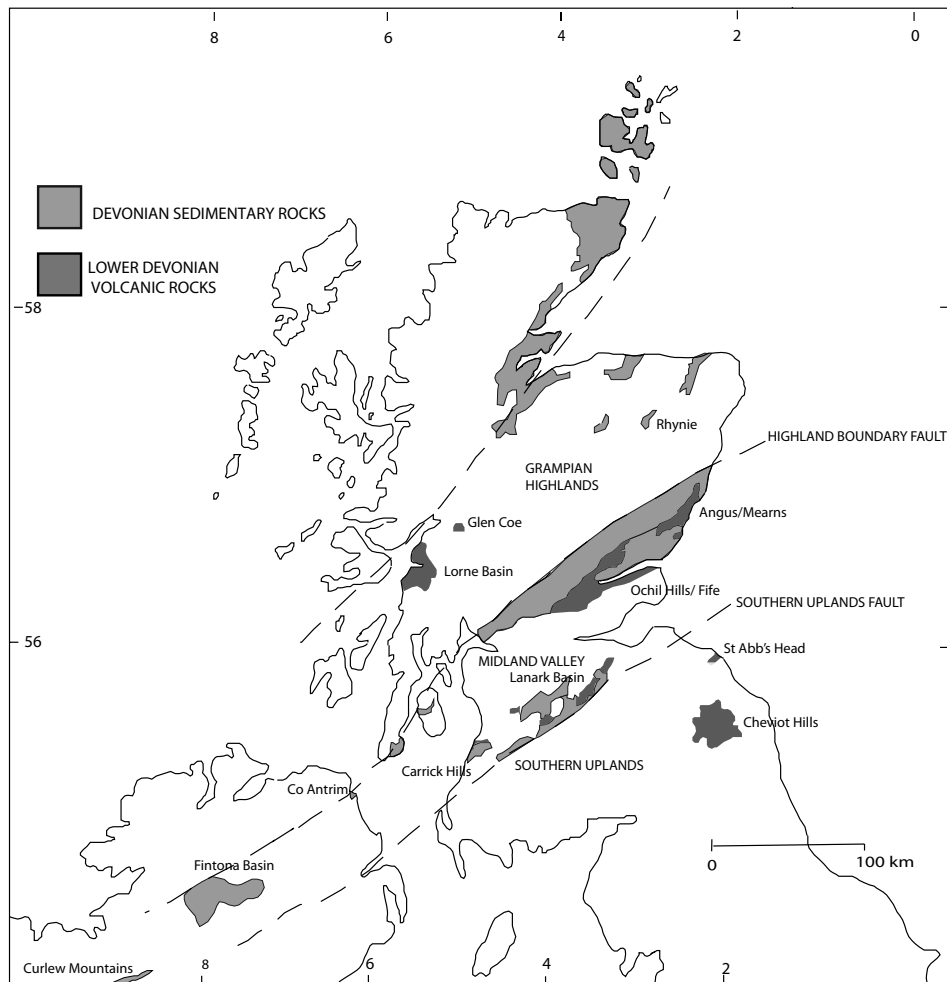
Figure 1   Map of northern British Isles showing Lower Devonian volcanic outcrops and sampling localities.

mutually consistent (Browne 1999). A review of the stratigraphy of Devonian volcanism in northern Britain (Smith 1999) similarly concludes that activity was focused in the Lochkovian.

The lava outcrops show a remarkable degree of similarity, including brecciation of lava flow surfaces, high vesicularity, and widespread reddening. They are typically the products of pāhoehoe flow-fields, forming units of up to 10m thickness, generally of the compound type, with individual pāhoehoe toes being in the range of 10–50 cm thick (Hole *et al.* 2013). These are interbedded with sedimentary rocks, some of which were deposited in minor lakes on top of the developing flow-fields. In general, compound pāhoehoe flow fields frequently develop pervasive weathered profiles, partly as a result of their vesicularity, but also because of the large surface area/volume ratio offered by their low aspect ratio (Self *et al.* 1998; Hole *et al.* 2013). Comparison with modern analogies suggests that the development of weathered profiles, and indeed the development of soil horizons, takes place in a matter of a few tens of thousands of years (Jolley *et al.* 2012). Weathering of the full thickness of pāhoehoe can occur because of vesicularity, and fracture permeability and, in many cases, the reddening is observed to extend a metre below the flow top.

The lavas typically show intermixing with sediments, including the penetration of sediment veins. In many cases, the magma is inferred to have been emplaced at a shallow level (<10 m) within unconsolidated sediments, rather than at the very surface (Kokelaar 1982; Smith 1995, 1999; Moore & Kokelaar 1998; Trewin & Thirlwall 2002). However, our observations suggest

that these features developed at the base of lava flows. A detailed assessment of lava-sediment interaction in the Lower Devonian is given in Hole *et al.* (2013). Pāhoehoe flow fields are punctuated and not continuous, such that during periods of no effusion, lakes develop on top of the flow-field, and fine-grain laminated sand and mud, some of which may be transported by aeolian processes, accumulates in the lakes. Resumption of effusive volcanism, before the sediment has lithified, and whilst it still contains significant pore-water, allows lava–sediment interaction to take place. Interaction occurs commonly at the base of individual pāhoehoe lobes, forming "peperite domains" with increasing sediment-to-lava ratio downwards from the base of the flow lobe (Skilling *et al.* 2002; Hole *et al.* 2013). In some cases, where sediment has undergone surface desiccation, lava lobes are unable to penetrate the desiccated sediment surface because the sediment no longer behaves as a viscous medium. However, where pore waters are still present at depth in the sediment pile (depths of only a few tens of centimetres), localised lateral and downwards invasion of lava into the wet sediment may occur. The outcrop expression of this phenomenon is the presence of a peperite domain on the upper surface of a lava lobe, with undisturbed sedimentary rocks resting directly on the peperite. This generic process is known from a number of localities worldwide, and the term "invasive lava flow" has been widely used in the literature, particular with respect to the Columbia River Basalt Province (e.g., Mangan *et al.* 1989; Ross 1989; Reidel 2005). The key point here is that whilst the lava is invasive, it is not intrusive, meaning that the invasion took place as a result of a subaerial
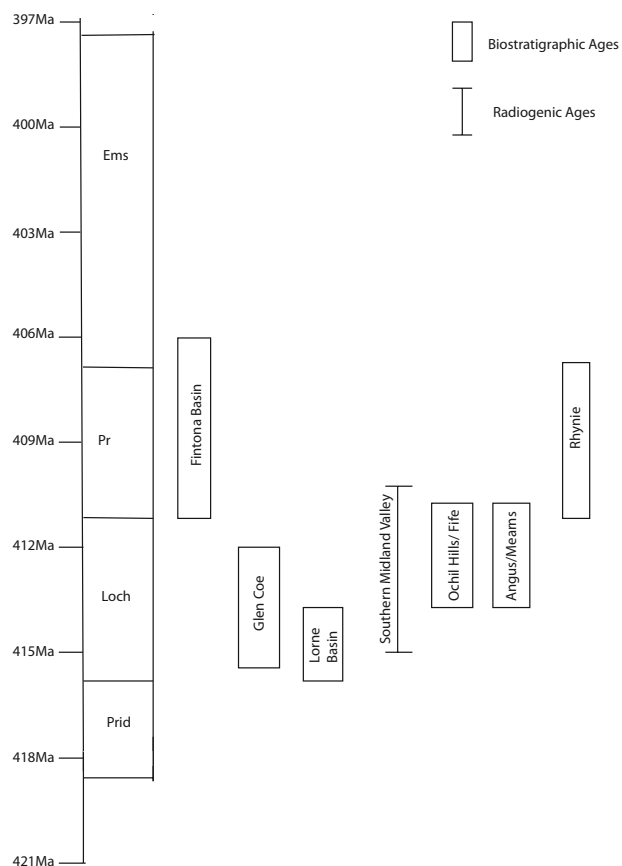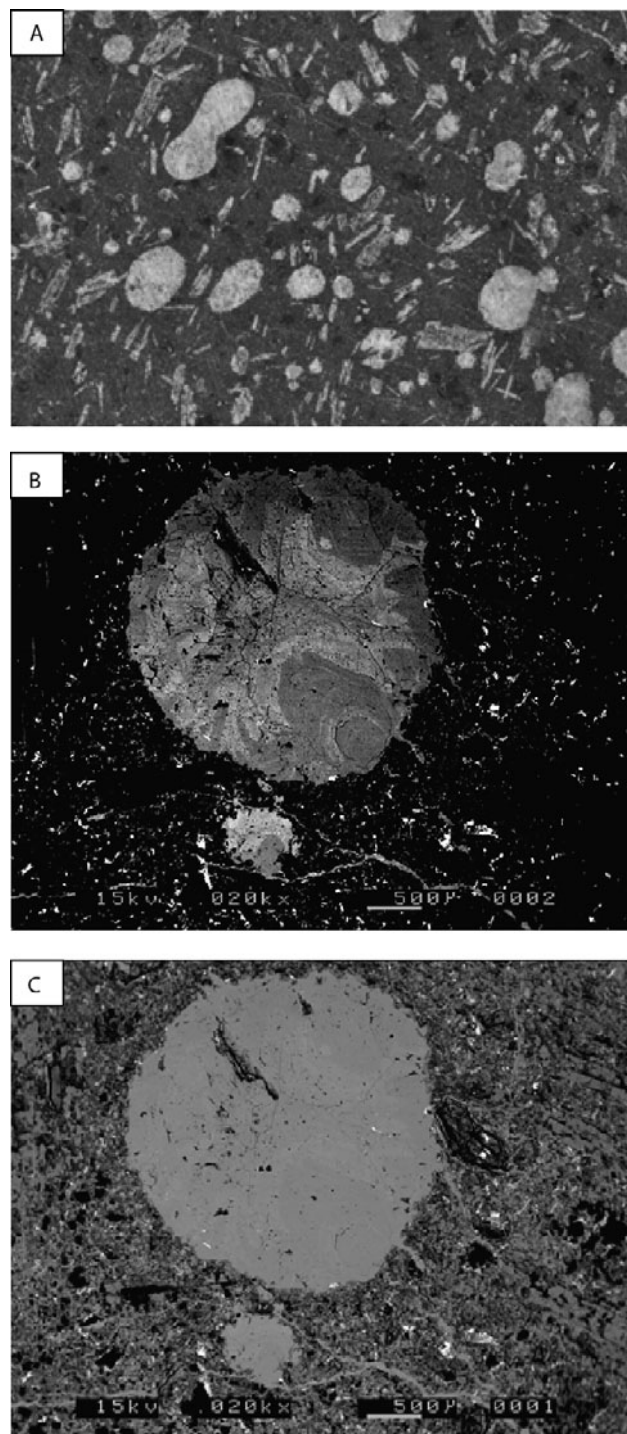
Figure 2 Age ranges for lava-bearing Lower Devonian sequences, determined from spore and radiometric dating. Integration of spore and radiometric dating from Mark *et al.* (2011), using timescale of Gradstein *et al.* (2005).


Figure 3 Images of calcite-filled vesicles in Lower Devonian lavas: (A) calcite-filled vesicles (round) and feldspar phenocrysts (laths) in altered basalt lava, Crawton, Mearns (field width 5 cm); (B)–(C) calcite-filled vesicle in lava, Dunstaffnage, Lorne Basin: backscattered electron image (B) shows zoning of infill due to variable manganese content. Secondary electron image (C) shows crenulate margins indicative of fluid–fluid (magma–wet sediment) intermingling during emplacement.

lava flow locally penetrating wet sediment. Consequently, even when invasive lava flows are present, lateral stratigraphical correlations show that the flow unit is dominantly subaerial.

The lavas were oxidised, and many flows are coloured red, purple or brown due to the alteration of iron minerals to haematite. The occurrence of fresh black lavas and red altered lavas in the same succession, and the co-occurrence of fresh and altered clasts of lava in conglomerates, both show that weathering was contemporaneous. Weathering of the lavas is also evident in the clay mineralogy of inter-bedded sedimentary units (Wilson 1971), and in a remanent magnetisation from low-temperature alteration of magnetic iron oxides (Storetvedt *et al.* 1992).

Calcite occurs as vesicle-fills (amygdales) (Fig. 3A), as interstitial infillings of autobrecciated lavas, and disseminated in the altered groundmass. Calcite occurs most abundantly in the more altered lavas, especially in those oxidised to a red colour. The calcite infillings of the vesicles were precipitated at a very early stage, as shown by: (i) their occurrence in clasts in immediately succeeding conglomerates; (ii) intermixtures of calcite and iron oxides in vesicles where the lavas experienced contemporaneous oxidation; and (iii) isotopic data for accompanying silica infillings and K-feldspar, which indicate low-temperature fluids with at least a partially meteoric origin (Fallick *et al.* 1985; Mark *et al.* 2011). Petrographic examination of the red, altered lavas shows a groundmass dominated by iron oxides and clay minerals, variable amounts of calcite, and corroded remnants of feldspar phenocrysts. Calcite vesicle-fills show growth zoning due to variations in manganese content (Fig. 3B). Less altered samples show serpentinisation of olivine, and chloritisation of the groundmass (Trewin & Thirlwall 2002). The vesicle-fills have very irregular margins, with crenulate

interfaces between calcite and host lava, and stringers of calcite penetrating the groundmass (Fig. 3C).

Samples from 12 localities were investigated for their carbonate content (Table 1). The samples are from lava, except those from Co. Antrim, where samples are from lava clasts in Lower Devonian conglomerates that are thought to be locally derived (Simon 1984a). The carbonate content was determined from samples of about 10 g, by measurement of mass loss following milling and dissolution in 10% hydrochloric acid. Where possible, both altered and unaltered lava samples were measured.

Table 1 Localities for carbonate measurement in Lower Devonian lavas

Region	Age	Lava thickness	Calcite %	n	Reference
Carrick Hills (Carrick Hills Formation)	410–415 Ma	400m	13.8	10	Kokelaar 1982; Browne *et al.* 2002
Lanark Basin (Duneaton Volcanic Formation)	410–415 Ma	600m	12.3	14	Mykura 1960; Browne *et al.* 2002
Ochil Hills/Fife (Ochil Volcanic Formation)	Lochkovian	2500m	12.6	16	Richardson *et al.* 1984
Angus/Mearns (Montrose Volcanic Formation)	Lochkovian	200m	12.6	10	Richardson *et al.* 1984
St. Abb' s Head (Eyemouth Volcanic Formation)	(Lower Dev.)	600m	17.6	10	Stephenson 1999
Cheviot Hills (Cheviot Volcanic Formation)	(Lower Dev.)	1000m	7.1	6	Carruthers *et al.* 1932
Glen Coe (Glencoe Volcanic Formation)	Lochkovian	1200m	8.5	10	Wellman 1994; Moore & Kokelaar 1998
Lorne Basin (Lorn Plateau Volcanic Formation)	early Lochk.	800m	23.3	17	Groome & Hall 1974
Co. Antrim (clasts in Cushendall Formation)	(Lower Dev.)	clasts	3.7	3	Simon 1984a
Fintona Basin (Fintona Group)	Pragian	500m	5.5	10	Simon 1984b; Stephenson & Mitchell 2002
Curlew Mountains (Keadew Formation)	(Lower Dev.)	600m	12.6	4	Charlesworth 1960; Graham & Clayton 1988
Rhynie (Tillybrachty Sandstone Formation)	Pragian	20m	2.1	3	Trewin & Rice 1992; Wellman 2006; Mark *et al.* 2011
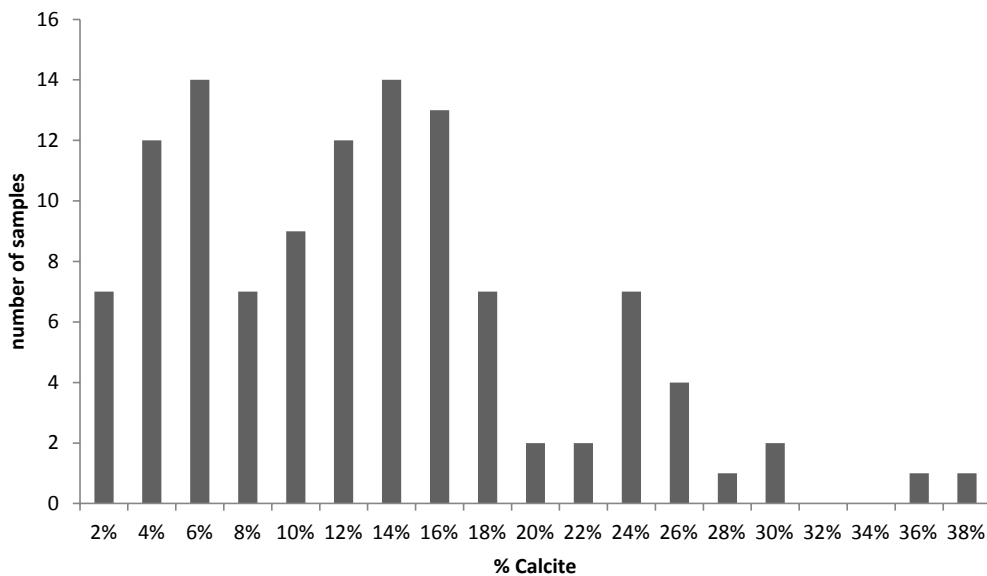
**Figure 4** Distribution of calcite contents (wt. %) in Lower Devonian lava samples.

2. Calcite contents of Devonian lavas

The total database for calcite contents in 104 samples is summarised in Figure 4. Samples from the Cheviot Hills were omitted from calculations, as their carbonate content is considered to be a consequence of hydrothermal alteration by post-lava granite intrusion. It is possible that lavas in other regions have experienced hydrothermal alteration, especially in Glen Coe (Moore & Kokelaar 1998) and Rhynie (Mark *et al.* 2011). However, the sampling was restricted to lavas in which the carbonate was limited to vesicles and autobreccias, and carefully avoided any lavas which exhibited carbonate (or other mineral) veining or brecciation typical of hydrothermal activity. The data show consistent high calcite contents across the region of study. The mean calcite content in altered lavas is 13%. The lavas show a wide range of calcite contents (Fig. 4); the higher values reflect calcite infillings of vesicles. In the most altered lavas, the highest calcite contents represent a combination of vesicle infilling and dissemination through the groundmass. A procedural blank (quartz sand) yielded 0.17% mass loss (mean of three samples), which was subtracted from the measured calcite loss.

3. Discussion

The calcite contents can be used to calculate the uptake of CO_2 into the lavas. One mole (44 g) of CO_2 is represented by 100 g of calcite. Assuming the mean calcite content in lavas of 13%, and a lava density of 2800 kg m^{-3}, a 1-m thickness of lava has sequestered 3.64×10^9 moles CO_2/km^2. Assuming a conservative 30% of lava was altered, and that originally the lava contained no calcite, the mean value for the 11 localities, weighted for lava thickness (mean thickness 675 m), is 7.3×10^{11} moles CO_2/km^2. Over the area of 100,000 km^2, this equates to 7.3×10^{16} moles CO_2. This will be an underestimate, because (i) in some localities the proportion of altered lava is clearly greater; (ii) inter-bedded sediments were also carbonated; (iii) we have not included highly auto-brecciated lavas (which contain more calcite) in our calculation; and (iv) modern weathering may have leached out some calcite.

The overall sequestration rate depends upon the time frame assumed. If we consider the whole Lochkovian–Pragian interval, lasting nine million years (Fig. 2), the mean sequestration rate is 8.1×10^9 moles/a. Volcanic activity in individual regions was probably of shorter duration, but also over a smaller area.
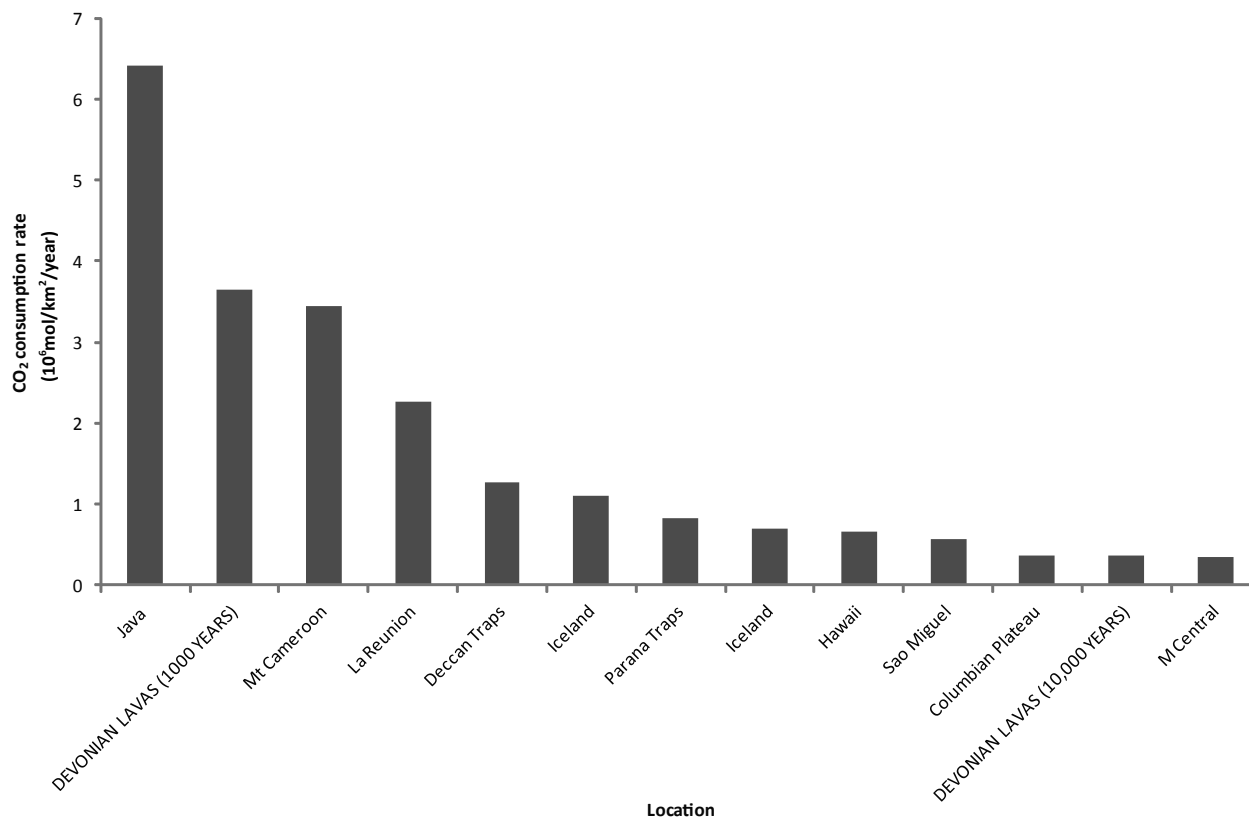
Figure 5 Consumption rate of CO_2 per unit area for modern basaltic provinces (data from Dessert *et al.* 2003) and Lower Devonian lavas. Devonian rates calculated for weathering to completion of a 1-m surface layer in 1000 and 10,000 years.

On a more local scale, sequestration rates could be higher. A 1-m thickness of weathering over 100 km² in ten years or one year would increase the rate by one or two orders of magnitude.

The area of 100,000 km² is a conservative estimate based on current outcrops in the northern British Isles. The extent of volcanic activity on the margin of the Iapetus Ocean would have been much greater. Lower Devonian basalts with reddened tops to flows are similarly recorded in Maine, USA (Gates & Moench 1981), indicating that the rapid subaerial alteration which promoted CO_2 drawdown occurred over a globally significant region. The altered region including Scotland and Maine represents approximately 2000 km of arc length (Cocks & Torsvik 2011).

The timescale over which drawdown occurred is uncertain. Baines & Worden (2004) suggest that solid phase CO_2 sequestration in deep sandstone reservoirs takes longer than tens to hundreds of thousands of years, controlled by the dissolution rate of reactive minerals. Sequestration in individual Devonian lava flows could have been much faster, due to more rapid fluid ingress in the near-surface, and consequent rapid alteration of minerals. Both auto-brecciation and magma–sediment interaction would promote alteration almost immediately upon extrusion. The hot magma would react with carbonate in the ambient ground waters. Thus, the irregular margins of calcite vesicle-fills, including stringers penetrating the groundmass, are fluid–fluid mingling textures which represent alteration while the rocks were solidifying. Such fluid–fluid mingling involves large surface areas for extensive and rapid alteration. In addition, these rocks were susceptible to carbonate mineralisation from shallow ground waters. In the prevailing climatic conditions, weathering and mineralisation may have penetrated several tens of metres. We estimate that at least 90% of the calcite in the Devonian lavas is sited in vesicles, as opposed to the altered groundmass. The vesicle-fills represent precipitation

from groundwater, while groundmass calcite is a result of fluid–rock interaction. Some samples of relatively fresh, black-coloured, lava contain vesicle-fill calcite, but no calcite in the groundmass. This implies that the vesicle infilling occurred first. However, both must take place rapidly, as red lava clasts in conglomerates contain both types of calcite. The close relationship of lavas, and conglomerates with lava pebbles, has been interpreted as a product of rapid reworking (Phillips 2007), probably in less than 1000 years. The preservation of blocky flow surfaces in some cases, rather than their erosion, has been interpreted to imply very rapid accumulation (Stephenson 1999), although it could also reflect the nature of lava emplacement.

We can make a comparison with modern CO_2 consumption in several ways: as a consumption rate per unit area; as consumption over the whole volcanic province; and consumption per unit length of volcanic arc. Comparison with the sequestration rate of modern provinces of volcanic rock is most appropriately made over the whole region.

Weathering of 13% of a 1-m surface layer consumes 3.64×10^9 moles/km². If that occurred over 1000 years, the consumption rate per unit area is 3.64×10^6 moles/km²/a. This is comparable to the highest rates determined from modern basaltic watersheds (Dessert *et al.* 2003; Fig. 5). Weathering over 10,000 years would still be comparable (Fig. 5), and weathering in less than 1,000 years would be much faster. Over the whole volcanic province in the northern British Isles, if the observed weathering is distributed over nine million years, the consumption rate for a weathered thickness of 200 m becomes 0.0081×10^{12} moles/a. That is about twice the consumption flux for the Greenland basaltic province (Cenozoic basalts in Greenland), of identical size (Dessert *et al.* 2003; Fig. 6). The Lower Devonian arc extended 4000 km westward down the eastern seaboard of modern North America (Cocks & Torsvik
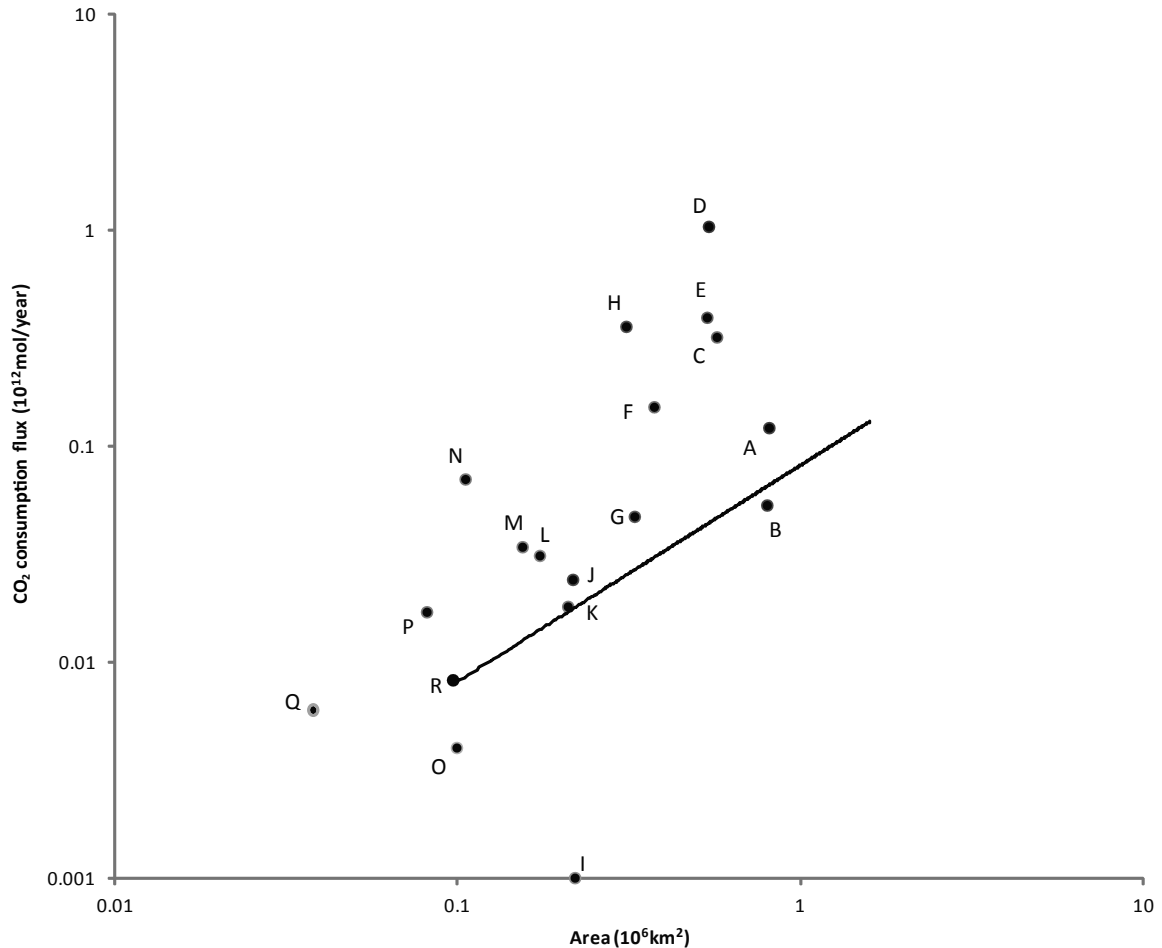
Figure 6 Plot of area against CO_2 consumption flux for modern basaltic provinces (data from Dessert *et al.* 2003) and Lower Devonian lavas: A = Ethiopia; B = Siberia; C = Parana; D = SE Asia/Indonesia; E = Deccan; F = Japan/East Russia; G = Australia; H = Central America; I = Arabian Peninsula; J = South Africa; K = Patagonia; L = Kamchatka; M = Columbia River; N = Iceland; O = Greenland; P = Cascade/Snake River; Q = East Canada; R = Devonian lavas. Flux for Devonian lavas also shown scaled upwards for increased area beyond British Isles.

2011) and, if we scale up the consumption flux proportionally for an increased area, it would be comparable with several other modern basaltic provinces (Fig. 6).

If the total consumption of 3.6×10^9 moles/a is distributed over about 500 km of volcanic arc in the northern British Isles, which was oriented parallel to the NE–SW structural grain (Cocks & Torsvik 2011), the consumption per unit length is 6.3×10^6 moles/km/a. This is comparable to the low end of the range of estimates for CO_2 output for modern volcanic arcs. James *et al.* (1999) predict a mean flux of 7.7×10^6 moles/km/a for the Cascadian volcanic arc, but other estimates for modern arcs are up to an order of magnitude greater (Gorman *et al.* 2006; Hilton *et al.* 2002). If we adopt the higher consumption rates for a smaller area, those rates would equal or exceed the output fluxes for modern arcs.

The process of sequestration by contemporaneous volcanism is clearly different to that of atmospheric weathering or artificial injection of ancient volcanic rocks. So why are these data valuable? First, they help us to understand the contribution of volcanic activity to the geological record of atmospheric CO_2 levels. The general assumption is that volcanism is a source, not a sink, of CO_2. Volcanoes today release up to 150 million tonnes (3.4×10^{12} moles) of CO_2 into the atmosphere each year (USGS 2010) from a combination of ocean ridge and arc volcanism. However, depending on the combination of timescale and arc length, the levels of drawdown that we have determined in the Devonian rocks can be comparable with or

exceed the CO_2 output flux. At least on a limited timescale, volcanic rocks may be self-compensating in their CO_2 budget. Secondly, the measurements give some indication of the natural capacity of volcanic rocks for CO_2 uptake. The same high porosity and permeability of lava flow tops makes them favourable for artificial sequestration (McGrail *et al.* 2006) and for geological sequestration, and also makes them good aquifers in many parts of the world (e.g. Russell & Rodgers 1977; Kulkarni *et al.* 2000). The vesicles in which much of the Devonian calcite occurs are also critical to artificially-induced calcite precipitation, as they present very large surface areas (McGrail *et al.* 2006). The calcite mineralogy is also intriguingly comparable, as both our Devonian examples (Fig. 3) and examples precipitated by laboratory experiment (McGrail *et al.* 2006) show zoning due to variable manganese content. Thirdly, atmospheric CO_2 levels were high during the Devonian (Berner 2006), but were falling rapidly to a much lower level in the Carboniferous. This accompanied the spread of photosynthesising plant life, but the abundant volcanic activity would have contributed to the uptake of CO_2.

4. Conclusions

The Lower Devonian lavas, distributed widely across the northern British Isles, show consistent evidence for contemporaneous subaerial weathering. The mineralogical alteration particularly involved the precipitation of calcite, representing

CO_2 drawdown from the atmosphere via groundwaters. Quantitative measurements of the calcite show that:

(i) The total drawdown over an area of 100,000 km^2 was in the region of 7×10^{16} moles CO_2;

(ii) distributed over the whole Lochkovian–Pragian interval of nine million years, this equates to a sequestration rate of 8×10^9 moles/a;

(iii) adopting shorter timescales for weathering suggests CO_2 consumption rates comparable to, or exceeding, those in modern basaltic watersheds;

(iv) the consumption rates per unit volcanic arc length equal or exceed output fluxes of CO_2 for modern arcs, showing that volcanic rocks can be an important net sink for CO_2.

5. Acknowledgements

6. References

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