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Silica-undersaturated trachytic rocks of central Scotland.

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Synopsis

The paper presents a review of silica-undersaturated salic intrusions (ne-normative trachytes and phonolites) from the Carboniferous-Permian magmatic province in central Scotland. New whole-rock major and trace element analyses, together with Sr and Nd isotopic data, are presented for six intrusions (Bass Rock, North Berwick Law, Traprain Law, Hairy Craig, Fintry and Loudoun Hill) and two syenite autoliths within the Loudoun Hill intrusion.

On the basis of the conventional total alkalis vs. silica diagram, all six intrusions are trachytes except for Traprain Law, which is a phonolite. Traprain Law is the most highly evolved and the most undersaturated in silica. The Loudoun autoliths are the most basic (Mg numbers of 21.8-27.3) and are inferred to be fragments of cumulates entrained at shallow crustal depths. Whilst all eight samples have approximately constant initial εNd *(+4.3 - +1.99), initial* $^{87}Sr/^{86}Sr$ *data are more variable (0.725929 – 0.709817). Although four of the samples have isotopic characteristics on, or close to, the Sr-Nd mantle array, those from Fintry, Bass Rock, Loudoun Hill and North Berwick Law lie at higher* $^{87}Sr/^{86}Sr_i$ *values, probably as a result of secondary alteration. From their petrographic and geochemical similarity, the six intrusions are considered to be products of a nearly identical petrogenesis,* *being late-stage residues from mildly silica-deficient basalt magmas, probably produced in 'underplated' chambers close to the crust–mantle boundary and subsequently intruded with minimal crustal interaction.*

Introduction

The Carboniferous and Permian igneous rocks of central and southern Scotland are predominantly basaltic and range from transitional to mildly alkaline to highly alkaline (Upton *et al*., 2004). A major suite of tholeiitic basic intrusions that was emplaced during Stephanian time is an exception. The most primitive members of the various suites range from quartz-hypersthene (*q-hy)-* to hypersthene *(hy)-* to nepheline (*ne)*-normative (Macdonald, 1975; Smedley, 1986). During the past thirty years petrological and geochemical attention has primarily been focussed on these more primitive rocks to the near-exclusion of the more-evolved rocks. More-evolved lavas in the range trachybasalt – trachyandesite – trachyte are restricted to the Tournaisian to mid-Visean sequences and there is a close spatial association between these lavas and intrusions of comparable, and even more-evolved, rock-types (Figure 1). Hence the evolved intrusions have been assumed to be of the same age as the evolved lavas. Younger magmatism (Late Visean to Permian), however, was, with the exception of the Stephanian quartz dolerite event, more magnesian than that of the earlier Carboniferous.

Most of the silicic rocks of the province are silica-saturated or over-saturated, defining a trend that leads to quartz-trachyte and, rarely, alkali rhyolite. However, those that are *ne*-normative (silica-undersaturated) define a separate trend towards phonolite. For those undersaturated compositions that are insufficiently silica-deficient to merit the term phonolite, we use the term phonolitic trachyte. The *ne*-

normative cases include several notable intrusions as well as some rare lavas of relatively evolved composition. Deuteric alteration and subsequent weathering commonly make petrographical description of the more-evolved rocks difficult and they commonly contain secondary quartz. Accordingly it is possible that other silica-undersaturated evolved rocks were emplaced but are now unidentifiable.

In the previous literature on the central and southern Scottish late Palaeozoic magmatism, the significance and even the existence of these two divergent petrological trends have generally not been recognised, even though they may have important implications for the magma genesis, evolution and age of the intrusions. Here we list all known phonolitic trachytes and phonolites in central and southern Scotland (Figure 1, Table 1), review most of the occurrences and present new data on six intrusions, including one of the largest, but least studied, the Loudoun Hill Plug, near Darvel in Ayrshire.

Carboniferous silica-undersaturated trachytic rocks of central and southern Scotland

Outcrops of Carboniferous and Permian igneous rocks in central and southern Scotland, excluding the Stephanian tholeiitic intrusions, are shown on Figure 1. All known occurrences of the more-evolved silica-undersaturated rocks (analcime trachyandesites, phonolitic trachytes and phonolites) are listed in Table 1 with references to previous literature. Such lavas are rare; two flows of analcime trachybasalt (not listed) are known from the Garleton Hills Volcanic Formation of East Lothian, while other relatively evolved lavas occur in the Clyde Plateau Volcanic Formation in the Dunlop–Eaglesham–Strathaven Uplands and the Campsie Fells.

The best known intrusions are those of the Bass Rock, North Berwick Law and Traprain Law in East Lothian (McAdam and Tulloch, 1985); Loudoun Hill and others around Darvel, a small intrusion at Fintry, close to the Campsie Fells and a cluster of smaller intrusions around Teviothead in the Southern Uplands complete the list. A glance at Figure 1 shows that all occurrences are closely associated spatially with Tournaisian to mid-Visean volcanic sequences, in particular the Clyde Plateau Volcanic Formation in the west, the Garleton Hills Volcanic Formation in the east and the Birrenswark Volcanic Formation in the south. There have been many detailed descriptions of the East Lothian intrusions, and in particular of the Traprain Law Laccolith (see Table 1 for complete list). There are also descriptions of the Teviot Head intrusions (McRobert, 1920) and of most of the intrusions in the Dunlop–Eaglesham–Strathaven area (Richey *et al*., 1930).

Traprain Law, long considered as a classic case of a laccolithic intrusion, has also been noted for the complex mineralisation along its joint planes (Williamson and Millward, 2003). Minerals recorded include analcime, anhydrite, apophyllite, datolite, natrolite, pectolite, prehnite, selenite, stilpnomelane, calcite and the molybdate, powellite (Battey and Moss 1962). This assemblage is inferred to have been precipitated from late-stage hydrous fluids at temperatures down to a few hundred degrees, containing sulphate, carbonate, halide and borate ions. Tomkeieff (1952) identified analcime trachybasalt inclusions in the Traprain Law intrusion.

Direct evidence for the age of the intrusions is lacking, although none of them is seen to cut strata younger than Visean. The only accepted radiometric dates available are from the Traprain Law intrusion and suggest a Visean age (De Souza, 1974, 1979).

The Loudoun Hill Plug

Surprisingly there are no published descriptions of the Loudoun Hill Plug, which, lying very close to the western edge of the Geological Survey Sheet 23, has been somewhat neglected. The memoir for this sheet was in preparation at the time of the outbreak of World War 2 but was never completed and the modern memoir for Sheet 23W (Paterson *et al*., 1998) gives no details. Fortunately a draft of the unpublished 1939 memoir, presumed to be by J. Phemister, survives in the archives of the British Geological Survey (BGS) in Edinburgh.

Loudoun Hill is a notable landmark, rising some 100 m above the surrounding glaciofluvial plain (Figure 2). The outcrop is ovoid in plan, elongated east–west and measuring 430 x 260 m. The western slopes are mantled by superficial deposits but the south flank is steep and craggy. Closely spaced joints parallel to a sub-vertical flow foliation suggest steeply inclined margins and Loudoun Hill almost certainly represents a sub-cylindrical plug that cuts basaltic lavas of the Clyde Plateau Volcanic Formation (Visean). Trachytic lavas occur nearby, at least one of which is silica undersaturated (Winkingfield, Table 1) and the plug may well have fed trachytic domes and associated pyroclastic eruptions at the surface.

Phemister's unpublished work described Loudoun Hill as consisting of trachybasalt (or trachyandesite), becoming finer grained towards the margin and cut in places by "shapeless pink syenitic veins and stringers". He wrote of "the normal rock" as containing sparse subhedral phenocrysts, up to 3 mm, of oligoclase and some andesine, containing patches of alkali feldspar or analcime. Microphenocrysts are of subhedral to euhedral purplish augite and of extensively resorbed hornblende replaced by aggregates of Fe-oxide and brown biotite. Phemister described the matrix as having a flow-structure involving oligoclase plus euhedral pyroxene, Fe-oxide, apatite and interstitial orthoclase and analcime. The sample representative of the host intrusion collected for this study differs from Phemister's "normal rock", in being a trachyte comprising alkali feldspar and clinopyroxene microphenocrysts together with opaque oxide-rich pseudomorphs, probably representing oxidised amphibole phenocrysts. Resolution of the problem relating to Phemister's trachybasalt and the trachyte taken by us requires a more detailed investigation of Loudoun Hill than we have been able to undertake in this reconnaissance study.

According to Phemister, a syenitic dyke with a maximum width of 1.2 m, on the north side of the hill, has idiomorphic oligoclase in a matrix of turbid orthoclase laths and abundant interstitial clear analcime. Pale green clinopyroxene, iron oxide, apatite and pseudomorphs after possible olivine were also noted. Narrow irregular veins of syenite occur south-west of the summit and all the syenites contain abundant xenoliths of the host trachybasalt/trachyandesite. In the same area, the host rock is permeated generally by syenitic material and grades into a pink syenite as orthoclase, analcime and natrolite become more abundant.

The present investigation has revealed that, in addition to being cut by syenitic veins, the Loudoun Hill host intrusion contains abundant small inclusions (up to ~ 10 cm) of coarse-grained syenite mainly made up of idiomorphic tabular crystals of feldspar, enclosing material that has preferentially dissolved during weathering leaving interstitial pits. Two samples (TR5 and TR6) were taken for further study since they have not previously been described. The reconnaissance study undertaken involved electron microprobe analysis of their principal components.

Analytical methods

Mineral and whole-rock analyses were made at the School of GeoSciences, University of Edinburgh. Mineral analyses were performed on a Cambridge Scientific Instruments Microscan 5 micro-analyser, using the wavelength dispersive method. Pure elements, oxides and simple silicate compositions were used as standards. Corrections were made for dead-time, atomic number, absorption and fluorescence using computer programs based on methods by Sweatman and Long (1969). The operating conditions were 20 kv and a sample current of 30 nA.

Whole-rock XRF analyses were carried out using a Philips PW 1480 spectrometer equipped with a Rh-anode tube. The instrument was calibrated using CRPG and USGS reference standards (Govindaraju, 1994). Major elements were determined on fused glass discs (Norrish and Hutton, 1969) with corrections applied for inter-element mass absorption effects. A full description of the techniques used is given in Fitton *et al*. (1998).

Rare-earth element (REE) analyses were conducted at the NERC ICP-AES Facility at Royal Holloway, University of London. Solutions were prepared using combined HF dissolution and alkali fusion as described in Walsh *et al*. (1981). Resultant solutions were analysed for rare-earth elements and selected potential interferences using a Perkin Elmer Optima 330-0RL ICP-AES.

Sr and Nd isotopes were analysed at the Isotope Geosciences Unit of the Scottish Universities Environmental Research Centre (SUERC), East Kilbride. Analytical procedures were similar to those described by Barbero *et al*. (1995). Total procedure blanks for Sr and Nd were < 300 pg. NIST SRM987 gave $^{87}Sr/^{86}Sr$ = 0.710254 ± 22 (2 SD, n = 34) and the internal laboratory Nd standard (JM) gave

$^{143}Nd/^{144}Nd$ = 0.511511 ± 8 (2 SD, n = 12) during this study. Rb, Sr, Sm and Nd were determined by isotope-dilution mass spectrometry.

Petrography and mineralogy of two Loudoun inclusions

Syenite sample, TR5, consists of alkali feldspar, clinopyroxene, feldspathoids, magnetite and apatite. The tabular feldspars, up to ~ 8 mm long, have highly sericitised cores and water-clear outer zones of sanidine containing crystallites of apatite. The sanidine displays no discernible exsolution and has simple carlsbad twins. Analysed feldspars have compositions varying from $An_{1.1}Cn_{0.2}Ab_{45.3}Or_{53.4}$ to $An_{0.7}Cn_{0.1}Ab_{43.8}Or_{55.4}$. Interstices between the feldspars contain pale creamy-yellow natrolite together with some analcime.

The pyroxenes occur as sub-idiomorphic prisms up to 2 mm long. In thin-section they are greenish grey, with the green colouration becoming slightly stronger in marginal zones. TiO_2 contents range from 1.04 to 0.59 wt% and Al_2O_3 contents from 1.17 to 0.62 wt%. Compositions vary from $Fs_{14.4}En_{39.6}Wo_{46.0}$ to $Fs_{20.0}En_{33.8}Wo_{46.2.}$ Magnetite is sub-idiomorphic to anhedral and shows marked exsolution with trellis-like lattices of magnetite and (altered) ilmenite. There is an abundance of slender “quench” needles of apatite up to 8 mm long, commonly tubular and some containing fluid inclusions.

The second sample, TR6, is texturally similar to TR5. It comprises clear sanidine showing carlsbad twins, much less sericitised than those in TR5. Compositions range from $An_{4.2}Cn_{0.6}Ab_{53}Or_{42.2}$ to $An_{1.6}Cn_{0.7}Ab_{45.3}Or_{52.4.}$ Interstitial material consists dominantly of yellow-brown sheaths of natrolite, with subordinate analcime. The clinopyroxene is greenish grey and is apparently unzoned. Compositions vary between $Fs_{15.0}En_{39.0}Wo_{46.0}$ and $Fs_{16.2}En_{36.7}Wo_{47.1.}$ TiO_2 contents range from 1.3 to 0.6%, whilst Al_2O_3 varies from 1.5 to 0.88 wt% and Na_2O from 0.9 to 0.6 wt.%. The magnetites are subhedral and up to ~ 1 mm across. Apatite, less abundant than in TR5, occurs as acicular prisms within the sanidines.

Although the TR5 and TR6 feldspars are all Ca-poor sanidines, the former are slightly more potassic than those of TR6. Both samples are ‘anhydrous’ with a notable absence of biotite and amphibole.

Whole-rock compositions

Table 2 shows eight new XRF analyses of silica-undersaturated silicic rocks from Central Scotland (the Loudoun Hill trachyte, the two studied autoliths and five other phonolitic trachytes from Fintry, the Bass Rock, North Berwick Law, Traprain Law and Hairy Craig). Previuosly published data on the compositions of salic rocks from the Midland Valley have depended primarily on wet-chemical analyses, dating from more than twenty-five years ago and which might not be directly comparable. A list of original sources of these analyses is given in Table 2. Most of the older analyses were also published by Guppy *et al*. (1931).

On the total alkali–silica (TAS) classification scheme of Le Bas *et al*. (1986), the Loudoun Hill host rock, Bass Rock, North Berwick Law, Hairy Craig and Fintry compositions are trachytes (Fig. 3). However, the Traprain Law sample lies in the phonolite field and the two syenitic inclusions from Loudoun Hill are tephri-phonolites. The Loudoun Hill trachyte has less K_2O (4.75 wt%) than the others and also the lowest values for Nb, Y, Rb, La, Ce, and Nd but it has the highest Ba content. Hairy Craig appears to be the least fractionated of the samples studied with the lowest Fe_2O_3*/MgO value (4.57) in comparison to much higher values for North Berwick

Law (18.9) and Traprain Law (23.6). It also has the highest P_2O_5, Ni, Cr, V, Cu and Zn contents of the six trachyte/phonolite samples.

The Loudoun Hill syenitic inclusions are regarded as comagmatic and accordingly will be described as autoliths. They have less SiO_2, Al_2O_3, MnO, Nb, Zr, La, Ce, Zn and Ba than the host trachyte but similar contents of Sr. They are correspondingly richer in MgO, CaO, TiO_2, P_2O_5, Cu, Ni, Cr and V. 100 x MgO/(MgO + Fe_2O_3) values for the autoliths are 21 – 28, as opposed to the 11 – 16 range for the trachytes.

Chondrite-normalised REE patterns (Fig. 4) for the Loudoun Hill host trachyte are very similar to those of its autoliths but with slightly more elevated LREE. The patterns for Traprain Law and the Bass Rock are also comparable to those for Loudoun Hill and there is near identity between the North Berwick Law and Hairy Craig patterns. The Fintry trachyte, however, has distinctly higher normalised REE values.

The six trachyte/phonolite patterns show only small negative Eu anomalies (most pronounced for North Berwick Law, Hairy Craig and Traprain Law). While this might imply little fractionation of Ca-bearing feldspar in their evolutionary history, this is contradicted by the behaviour of major elements and Sr in the province (Smedley, 1986). Smedley listed various lines of evidence pointing to the magmas having evolved under relatively oxidising conditions (with high P_{H2O}) and suggested that the Eu was therefore largely in the trivalent rather than divalent state. Thus it tended not to substitute for Ca^{2+} in plagioclase to produce a negative Eu anomaly. The two Loudoun autoliths also lack a discernible Eu anomaly.

In the absence of better age constraints, initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ (and ε_{Nd}) are calculated at 300 Ma (Table 3) but uncertainties in the precise age-correction are unlikely to undermine our interpretation of the data. All samples have fairly constant ε_{Nd} but variable initial $^{87}Sr/^{86}Sr$, such that they define a horizontal trend on the Sr-Nd isotope diagram (Fig. 5). TR3, TR5, TR6 and TR8 fall on or close to the Sr-Nd mantle array but TR1, TR2, TR4 and TR7 lie off the array at elevated $^{87}Sr/^{86}Sr$. Such characteristics are rarely observed in fresh igneous rocks and the range in $^{87}Sr/^{86}Sr$ and roughly constant ε_{Nd} is likely best attributed to either (1) an under-correction of initial $^{87}Sr/^{86}Sr$ in the higher $^{87}Sr/^{86}Sr$ samples due to post-eruption Rb-loss through alteration or (2) by increased present-day $^{87}Sr/^{86}Sr$ through post-eruption exchange with high $^{87}Sr/^{86}Sr$ hydrothermal fluids.0

Origin of the Loudoun Hill autoliths

The syenitic inclusions at Loudoun Hill are presumed to be cognate and intimately related to the host trachytic magma. It may be inferred (from the low alumina content of the pyroxenes and the presence of analcime and natrolite) that the source-rocks from which the autoliths were derived lay at relatively shallow depths. The unconformity between the high-grade mid-crustal gneisses and the overlying cover of Palaeozoic strata (at ~ 7km depth: Upton et al., 1983 and references therein) is one likely level at which ascending magma may have been arrested to form a sill or laccolith. The autoliths probably represent fragments of side-wall cumulates entrained as the host magma ascended.

The minerals in TR5 are slightly more evolved than those of TR6 suggesting that the autoliths were derived from an inhomogeneous and somewhat differentiated source. The syenitic magma is inferred to have had a composition close to the sanidine-salite cotectic. Nepheline is likely to have crystallised in the interstices at high temperature and to have been subsequently replaced by analcime and finally by natrolite. Quench apatites in the autoliths are commonly hollow with a cavity along the length of the crystal. The extremely acicular apatite crystals grew early enough to be enclosed by the sanidine. Their morphology points to very rapid growth (Wyllie *et al*., 1962), possibly triggered by an early phase of volatile release. Certainly the lack of any hydrous ferromagnesian minerals suggests a relatively anhydrous magma, although the growth of zeolites clearly indicates concentration of hydroxyl ions and water at the latest crystallisation stage.

The two syenitic autoliths are richer in ferromagnesian components than their host trachyte. That they contain higher concentrations of compatible-elements and concomitantly lower contents of incompatible-elements may imply that they are accumulitic, having lost some of their more fractionated residual intercumulus melts.

Origin and evolution of the Midland Valley silica-undersaturated magmas

Although the phonolitic rocks have been assigned traditionally to the Tournaisian to mid-Visean volcanic activity with which they are spatially associated, their silica-undersaturated nature is somewhat anomalous. From the late Visean through to the Early Permian, with few notable exceptions (e.g. the late-Carboniferous tholeiitic suite), the most primitive basalts in central Scotland became progressively more silica undersaturated (Macdonald *et al*., 1977). Smedley (1986) remarked on the close association between *ne*- and *hy*-normative compositions in the Early Carboniferous lava sequences and pointed out that evolution of the suite as a whole could not have occurred at low pressures because the compositions cross the critical plane of silica saturation. There has been general consensus (Macdonald, 1975; MacDonald and Whyte, 1981; Russell, 1985) that magmatic evolution took place under polybaric conditions, with some fractionation commencing at mantle depths (> 13 kbar).

Apart from those with the highest initial $^{87}Sr/^{86}Sr$ that are thought likely to reflect post-emplacement processes, the samples plot close to the Sr-Nd mantle array with initial ε_{Nd} of +2.0 to +4.3. Such values are indicative of a strong mantle influence. Either the magmas were derived from a depleted mantle source and then affected by small-degree crustal contamination or they were derived from more-enriched mantle that subsequently experienced negligible crustal contamination. In view of the alkalic nature of likely parental magmas, and the likelihood that such magmas would have $^{143}Nd/^{144}Nd$ ratios less than those of mid-ocean ridge basalts, we are inclined to favour the latter option. However, we would stress that the available data do not provide definitive evidence in favour of either option.

Silica-poor alkali basalts and basanites were erupted in the younger Carboniferous (Silesian) and Early Permian magmatism, represented in e.g. the Mauchline Volcanic Formation and associated intrusions in Ayrshire and by numerous plugs and diatremes in East Fife and East Lothian. Since Loudoun Hill and the East Lothian intrusions could be regarded as spatially within, or peripheral to, these two volcanic fields, the possibility of their having a Late Carboniferous to Early Permian age should be considered. However, the evidence suggests that these younger and more highly silica-undersaturated basic magmas were produced in such small volumes that substantial magma chambers were not produced and accordingly salic differentiates were wholly insignificant (Upton *et al*., 2004). The balance of probability remains that the phonolitic trachytes and phonolites under consideration were residual products of the much more-voluminous mildly alkalic basaltic magmas and that siliceous mid- to upper-crustal rocks was minimal.

These residual salic compositions tended to be erupted late with respect to the bulk of the Dinantian magmatism of the Lothians and the Clyde Plateau; the lateness probably reflects the extended time required for the requisite degree of fractional crystallisation. The phonolitic trachytes and phonolites of the Midland Valley have sufficient compositional affinity for it to be a reasonable assumption that they resulted from similar petrogenetic processes and that they are likely to have been roughly contemporaneous. Although the Traprain Law phonolite magma represented the most extreme composition, the absence of nepheline phenocrysts indicates that it failed to reach the alkali-feldspar–nepheline phase boundary in 'the residua system' $CaAl_2Si_2O_8$-$NaAlSiO_4$-$KAlSiO_4$-SiO_2 (Carmichael *et al.*, 1974).

That the rocks under consideration retained their silica-undersaturated nature to shallow levels implies that their magmas experienced little crustal assimilation and hence that their ascent was relatively rapid and unhindered. None the less, the syenite autoliths in the Loudoun intrusion, regarded here as shallow crustal sidewall cumulates, may indicate formation of a small magma chamber at a depth of a few kilometres.

Whilst this paper presents some modern data on rocks that have been little studied during the past fifty years, we would emphasize the desirability of a much more comprehensive investigation of the Lower Carboniferous salic intrusions, including all those of the Southern Uplands and Kintyre as well as those of the Midland Valley.

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References

BARBERO, L., VILLASECA, C. ROGERS, G. & BROWN, P.E. 1995. Geochemical and isotopic disequilibrium in crustal melting: An insight from the anatectic granitoids from Toledo, Spain. *Journal of Geophysical Research*, **100**, 15,745-15,765.

BATTEY, M. H. & MOSS, A. A. 1962. Powellite from Traprain Law, Haddingtonshire, Scotland. *Mineralogical Magazine*, **33**, 158-161.

BENNETT, J.A.E. 1945. Some occurrences of leucite in East Lothian. *Transactions of the Edinburgh Geological Society*, **14**, 34 – 52.

CARMICHAEL, I.S.E., TURNER, F. J. & VERHOOGEN, J. 1974. Igneous Petrology, McGraw-Hill Book Company, New York.

CLOUGH, C.T., HINXMAN, L.W., WILSON, J.S.G., CRAMPTON, C.B., WRIGHT, W.B., BAILEY, E.B. & CARRUTHERS, R.G. 1925. *The geology of the Glasgow district* (2nd edition). Memoir of the Geological Survey of Great Britain, parts of sheets 30, 31, 22 and 23 (Scotland).

CRAIG, P.M. 1980. *The volcanic geology of the Campsie Fells area, Stirlingshire*. Unpublished PhD thesis, University of Lancaster.

DE SOUZA, H. A. F. 1974. *Potassium-argon ages of Carboniferous igneous rocks from East Lothian and the south of Scotland.* Unpublished MSc thesis, Unversity of Leeds.

DE SOUZA, H. A. F. 1979. *The geochronology of Scottish Carboniferous volcanism.* Unpublished PhD thesis, University of Edinburgh.

FITTON, J. G., SAUNDERS, A. D., LARSEN, L.-M., HARDARSON, B. S. & NORRY, M. J. 1998. Volcanic rocks from the southeast Greenland margin at 63°N: composition, petrogenesis and mantle sources. In: *Proceedings of ODP Scientific Results* ***152*** (eds. A. D. Saunders, J. C. Larsen and S. H. Wise), pp 331-350, College Station, TX.

GOVINDARAJU, K. 1994. 1994 compilation of working values and sample description for 383 geostandards. Geostandards Newsletter, **18**, 1-158.

GUPPY, E.M., THOMAS, H.H., ENNOS, F.R. & SUTCLIFFE, R. 1931. *Chemical analyses of igneous rocks, metamorphic rocks, and minerals*. Memoir of the Geological Survey of Great Britian.

HATCH, F. H. 1892. A new British phonolite. *Geological Magazine*, New Series, Decade lll, **9**, 149-150.

LE BAS, M.J., LE MAITRE, R.W., STRECKEISEN, A. & ZANETTIN, B. 1986. A chemical classification of volcanic rocks based on the total alkali – silica diagram. *Journal of Petrology*, 27, 745-750.

LUMSDEN, G.I., TULLOCH, W., HOWELLS, M.F. & DAVIES, A. 1967. *The geology of the neighbourhood of Langholm*. Memoir of the Geological Survey of Great Britain, Sheet 11 (Scotland).

McADAM, A. D. & TULLOCH, W. 1985. *Geology of the Haddington District,* Memoir of the British Geological Survey, Sheet 33W and part of 41 (Scotland),.

MacDONALD, J. G. & WHYTE, F. 1981. Petrochemical evidence for the genesis of a Lower Carboniferous transitional basaltic suite in the Midland Valley of Scotland. *Transactions of the Royal Society of Edinburgh, Earth Sciences,* **72**, 75-88.

MACDONALD, R. 1975. Petrochemistry of the early Carboniferous (Dinantian) lavas of Scotland. *Scottish Journal of Geology*, **4**, 269-314.

MACDONALD, R., THOMAS, J.E. & RIZZELLO, S.A. 1977. Variations in basalt chemistry with time in the Midland Valley province during the Carboniferous and Permian. *Scottish Journal of Geology*, **13**, 11-22.

MacGREGOR, A. G., & ENNOS, F. R., 1922. The Traprain Law phonolite. *Geological Magazine*, **59**, 514-523.

McROBERT, R.W. 1920. Igneous rocks of the Teviot and Liddesdale. *Transactions of the Edinburgh Geological Society*, **11**, 86-103.

MARTIN, N.R. 1955. Lower Carboniferous volcanism near North Berwick. *Bulletin of the Geological Survey of Great Britain*, **7**, 90-100.

NORRISH, K. & HUTTON, J. T. 1969. An accurate spectrographic method for the analysis of a wide range of geological samples. *Geochimica Cosmochimica. Acta* **33**, 431-453.

PATERSON, I.B., McADAM, A.D., & MacPHERSON, K.A.T. 1998. *Geology of the Hamilton District*. Memoir of the British Geological Survey, Sheet 23W (Scotland).

RICHEY, J.E., ANDERSON, E.M., MACGREGOR, M.C. 1930. *The Geology of North Ayrshire (explanation of one-inch sheet 22).* Memoir of the Geological Survey of Scotland. D.S.I.R.

RUSSELL, D.G. 1985. *Experimental and petrological studies of phenocryst assemblages in Scottish Permo-Carboniferous basaltic rocks*. Unpublished PhD thesis, University of Edinburgh.

SWEATMAN, T. R. & LONG, J. V. P. 1969. Quantitative electron microanalysis of rock-forming minerals. *Journal of Petrology*, **10**, 332-379.

SMEDLEY, P.L. 1986. *Petrochemistry of Dinantian volcanism in northern Britain.* Unpublished PhD thesis, University of Edinburgh.

SUN, S.-S & MCDONOUGH, W.F. 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *In* Saunders, A.D. & Norry, M.J. (eds) *Magmatism in the Ocean Basins*, Geological Society, London. Special Publications, **42**, 313–345.

TOMKEIEFF, S. I. 1952. Analcite-trachybasalt inclusions in the phonolite of Traprain Law. *Transactions of the Edinburgh Geological Society,* **15**, 360-373.

UPTON, B.G.J., ASPEN, P. & CHAPMAN, N.A. 1983. The upper mantle and deep crust beneath the British Isles: evidence from inclusions in volcanic rocks. J. geol. Soc. London, **140**, 105-121.

UPTON, B.G.J., STEPHENSON, D., SMEDLEY, P.M., WALLIS, S. M. & FITTON, J.G. 2004. Carboniferous and Permian magmatism in Scotland. Journal of the Geological Society of London, Special Publication '*Carbo-Permian Magmatism in Western Europe*', (eds. Wilson, M., Neumann, E-R, Davies, G.R., Timmerman, M.J., Heeremans, M & Larsen B.T.) 195-218.

WALSH, J. N., BUCKLEY, F. & BARKER, J. 1981. The simultaneous determination of the rare-earth elements in rocks using Inductively Coupled Plasma Source Spectrometry. *Chemical Geology*, **33**, 141-153.

WILLIAMSON, I.T. & MILLWARD, D. 2003. Traprain Law, East Lothian. In: *Carboniferous and Permian Igneous Rocks of Great Britain North of the Variscan Front* D. Stephenson, S. C. Loughlin, D. Millward,, C. N. Waters and I.T. Williamsons (eds). *Geological Conservation Review Series*, 60-64.

WYLLIE, P.J., COX, K.G. & BIGGAR, G.M. 1962. The habit of apatite in synthetic systems and igneous rocks. *Journal of Petrology*, **3**, 238-243.

Figure captions

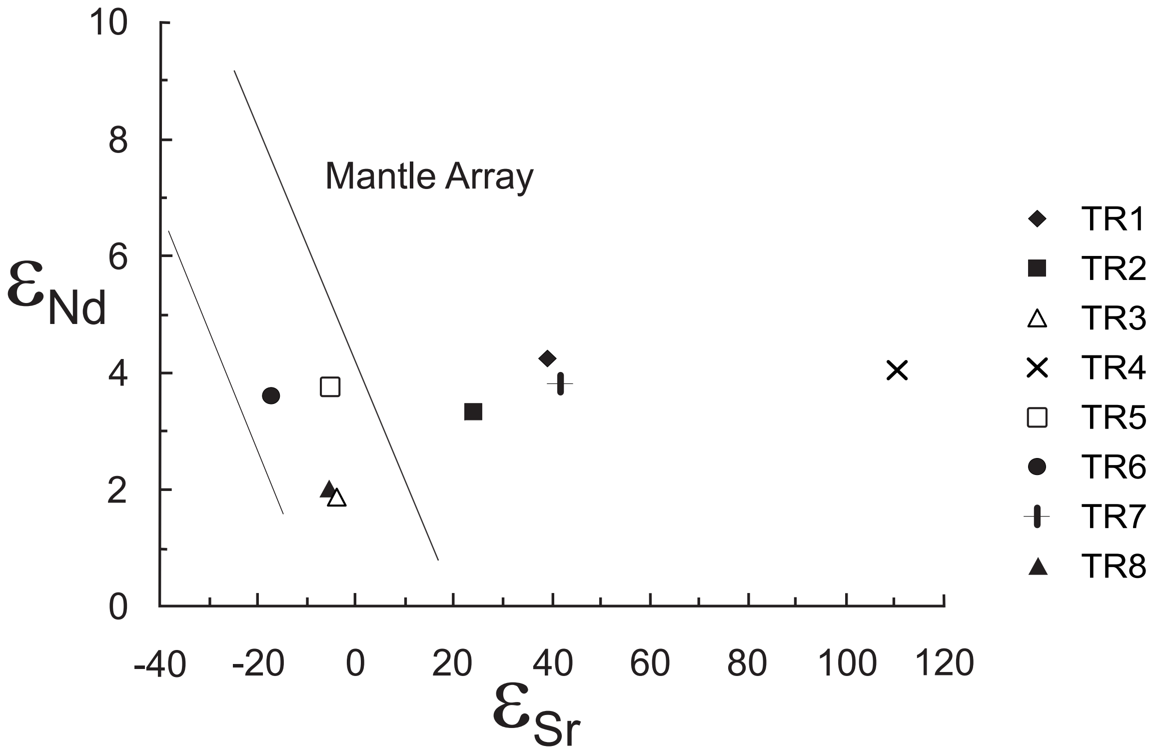
Fig. 1. Sketch map showing location of Loudoun Hill and other phonolitic trachytes in central and southern Scotland. Intrusions: BR Bass Rock, BL North Berwick Law, F Fintry, HC Hairy Craig, LH Loudoun Hill, LS Laird's Seat, M Mearns, P Priestland, TG Townhead of Grange, TH Teviothead, TL Traprain Law, U Underlaw. Lavas: +.

Fig.2. Loudoun Hill from the southwest. (British Geological Survey photograph No: P 64463, reproduced with the permission of the Executive Director, British Geological Survey, © NERC.)

Fig. 3. Total alkali *vs*. silica (TAS) diagram after Le Bas *et al*., 1986. Filled symbols are new analyses. Abbreviations for intrusions as in Figure 1. Lavas: BH, Blaikie Heugh; FG, Fin Glen; H, Halket; W, Winkingfield.

Fig. 4. Chondrite-normalised rare-earth element patterns for the six analysed trachytes and two syenite autoliths from central Scotland. Normalising factors from Sun & McDonough (1989).

Fig. 5. εNd vs εSr (calculated at 300 Ma) for the eight trachytic rocks and two syenite autoliths, compared to the mantle array for oceanic basalts. Symbols as in Figure 4.



10
8
6
4
2
0
ε_{Nd}
Mantle Array
-40
-20
0
20
40
60
80
100
120
ε_{Sr}
TR1
TR2
TR3
TR4
TR5
TR6
TR7
TR8

Table 3 Rb-Sr and Sm-Nd isotopic data

	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8
$^{87}Sr/^{86}Sr_{(0)}$	0.718438	0.721138	0.717747	0.709817	0.709469	0.710216	0.725929	0.710488
	+/- 17	+/-25	+/-22	+/-17	+/-18	+/-21	+/-17	+/-17
$^{87}Rb/^{86}Sr$	2.667	3.543	3.208	1.320	1.293	1.670	4.372	1.528
$^{87}Sr/^{86}Sr_{(300)}$	0.707049	0.706012	0.704053	0.712112	0.703949	0.703087	0.707265	0.703964
ε_{Sr}	+38.5	+23.8	-4.1	+110.4	-5.5	-17.8	+41.6	-5.3
$^{143}Nd/^{144}Nd_{(0)}$	0.512704	0.512587	0.512514	0.512654	0.512675	0.512676	0.512662	0.512511
	+/-8	+/-6	+/-6	+/-17	+/-7	+/-11	+/-7	+/-6
$^{147}Sm/^{144}Nd$	0.118726	0.083694	0.084225	0.100014	0.117744	0.121838	0.109045	0.080098
$^{143}Nd/^{144}Nd_{(300)}$	0.512471	0.512423	0.512349	0.512458	0.512444	0.512437	0.512448	0.512354
ε_{Nd}	+4.3	+3.3	+1.99	+4.0	+3.7	+3.6	+3.8	+2.0

Initial ratios and epsilon values calculated at 300 Ma using isotope dilution trace-element determinations by thermal ionization mass spectrometry.

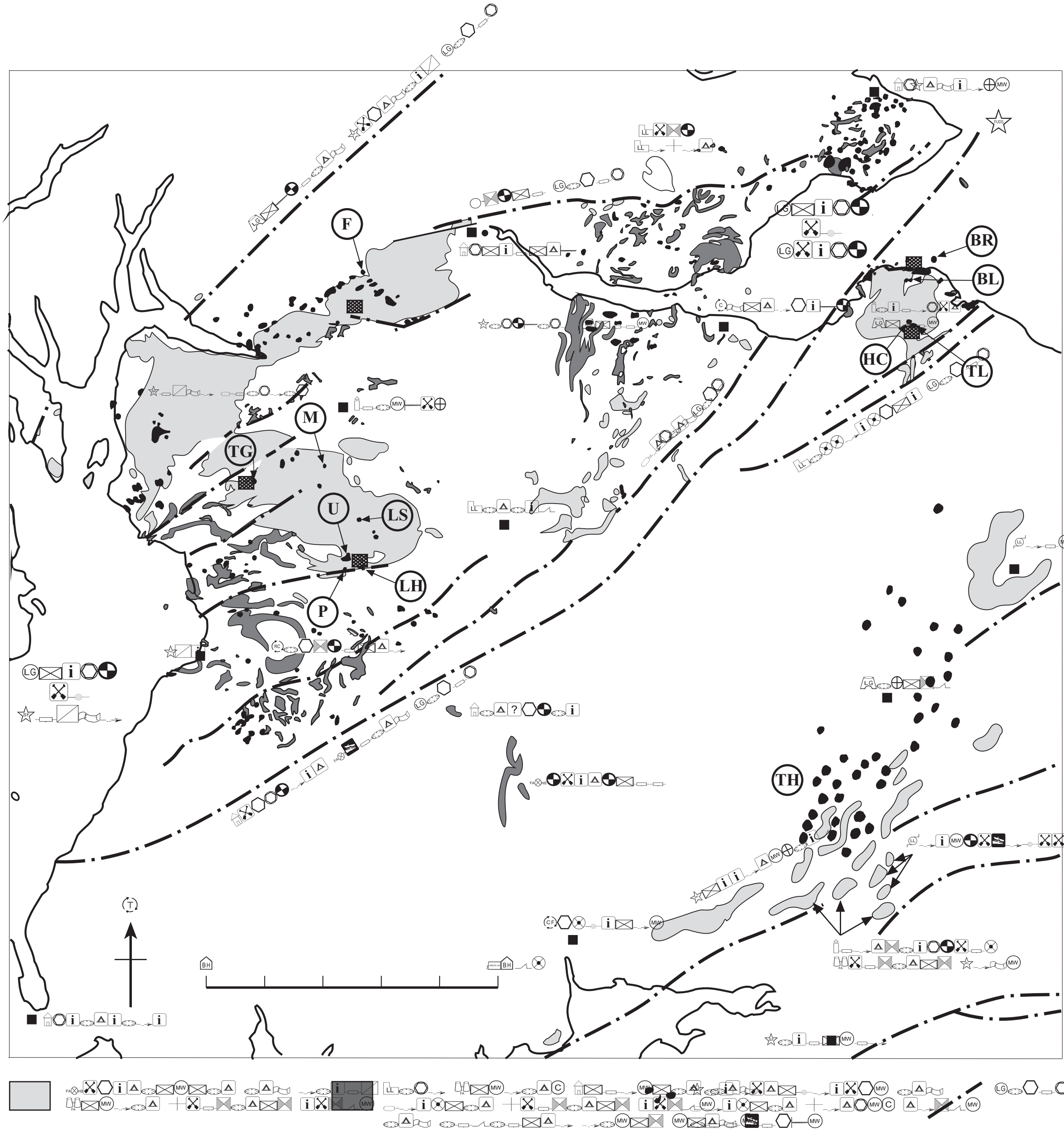

F
M
TG
U
LS
LH
P
BR
BL
HC
TL
TH
BH

Table 2 New analyses of evolved, silica-undersaturated volcanic and intrusive rocks of Carboniferous to Permian age in Scotland

Wt %	**TR1**	**TR2**	**TR3**	**TR4**	**TR5**	**TR6**	**TR7**	**TR8**
SiO_2	59.32	59.17	57.20	60.48	55.04	55.66	60.90	59.45
TiO_2	0.13	0.45	0.35	0.36	1.49	1.51	0.38	0.47
Al_2O_3	17.45	16.66	18.44	17.81	15.87	15.06	17.90	19.32
Fe_2O_{3TOT}	6.77	7.27	5.79	5.46	6.81	6.80	5.48	3.70
MnO	0.13	0.12	0.19	0.14	0.10	0.11	0.15	0.08
MgO	1.25	1.10	0.25	0.69	1.90	2.55	0.29	0.81
CaO	0.70	1.52	1.88	1.22	3.74	4.63	1.71	1.72
Na_2O	6.12	5.11	7.25	6.88	5.13	5.26	6.42	4.17
K_2O	5.31	6.25	5.92	4.75	6.30	5.80	5.82	7.06
P_2O_5	0.07	0.12	0.13	0.13	0.49	0.33	0.08	0.16
LOI	2.21	1.64	2.02	1.49	2.50	1.98	1.02	3.11
Total	99.46	99.41	99.42	99.41	99.37	99.69	100.15	100.05
ppm								
Ni					7	9	2	4
Cr	1	1	2	1	14	21	3	6
V					32	64		1
Sc	4	8	3	4	8	8	2	
Cu	5	10	6	6	34	23	11	12
Zn	187	179	114	128	67	60	102	58
Rb	142	131	196	112	117	99	136	167
Ba	544	590		888	324	211	286	517
Sr	147	112	192	267	270	199	100	360
Zr	978	468	635	749	317	230	576	561
Nb	163	117	179	103	64	43	116	154
Y	84	45	29	24	27	22	50	31
ppm								
La	104.00	36.80	52.50	30.70	25.20	16.10	64.00	70.00
Ce	218.50	68.00	89.00	57.30	51.40	35.20	131.00	146.00
Pr	21.90	6.60	8.50	5.40	5.00	3.30	14.10	15.60
Nd	107.00	29.00	26.90	20.30	23.30	16.20	55.30	62.00
Sm	20.85	5.26	4.13	3.38	4.69	3.27	9.67	11.10
Eu	4.78	1.34	0.81	0.80	1.14	0.92	1.79	1.82
Gd	17.51	4.48	2.95	2.51	3.81	2.65	8.05	9.09
Dy	16.59	3.58	2.35	1.95	2.57	2.03	7.25	7.87
Ho	3.31	0.83	0.64	0.51	0.52	0.43	1.45	1.63
Er	8.27	1.96	1.45	1.07	1.14	1.04	3.83	4.28
Yb	6.92	1.73	1.27	0.78	0.77	0.87	4.03	4.75
Lu	1.14	0.28	0.21	0.13	0.12	0.14	0.66	0.75
norm:								
q	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.98
ne	0.95	0.00	14.85	2.14	8.47	8.75	3.91	0.00
hy	0.00	0.56	0.00	0.00	0.00	0.00	0.00	6.16

TR1	phonolite	intrusion	Fintry	Strath Blane	this work
TR2	phonolitic trachyte	plug	Bass Rock	E Lothian	this work
TR3	phonolite	laccolith	Traprain Law	E Lothian	this work
TR4	phonolitic trachyte	plug	Loudoun Hill	Darvel	this work
TR5	syenite	xenolith	Loudoun Hill	Darvel	this work
TR6	syenite	xenolith	Loudoun Hill	Darvel	this work
TR7	phonolitic trachyte	plug	N Berwick Law	E Lothian	this work
TR8	phonolite	sheet	Hairy Craig	E Lothian	this work

Previously published analyses

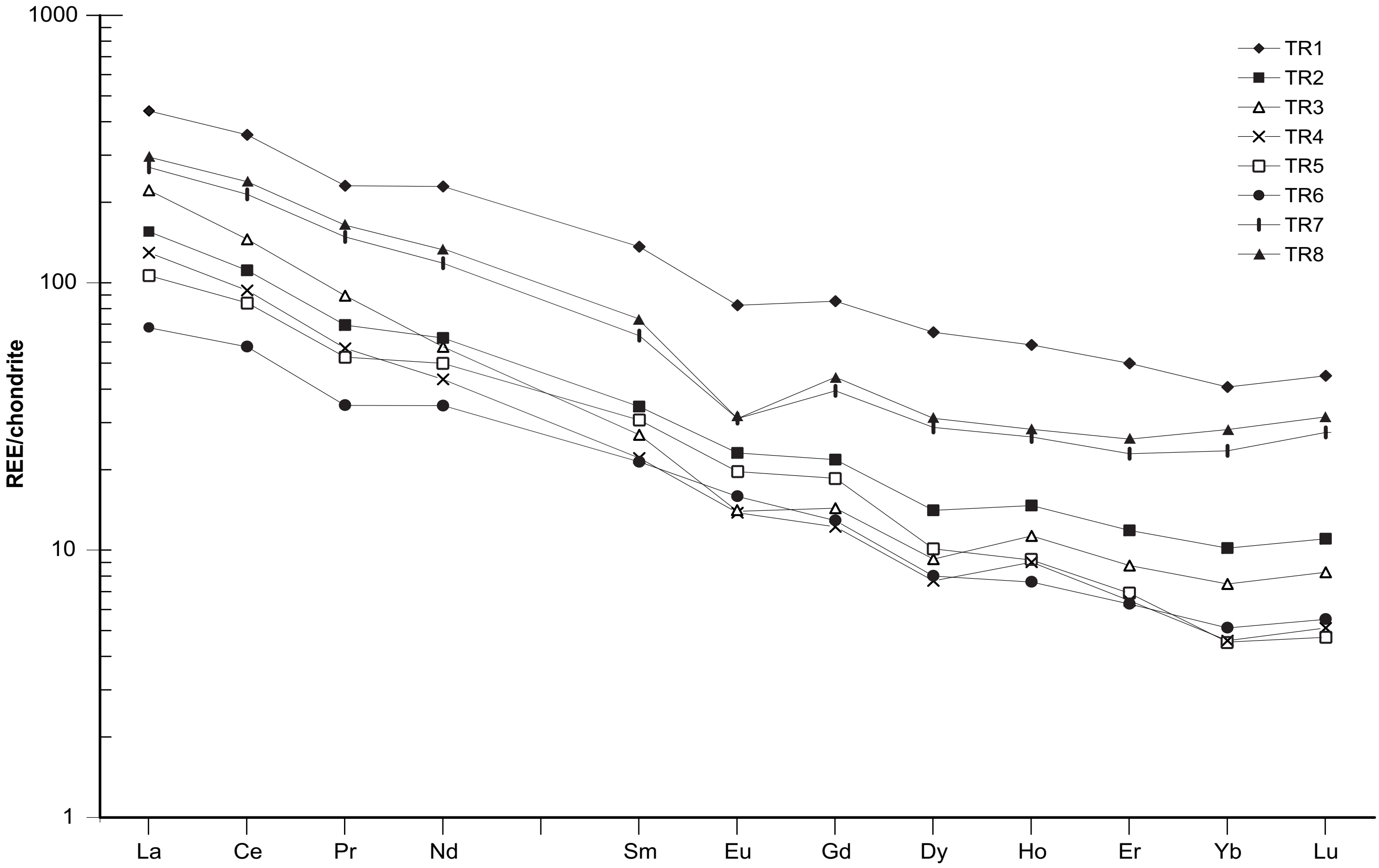
1	phonolitic trachyte	lava	Dunbrach	Campsie Fells	MacDonald & Whyte 1981	
2	phonolitic trachyte	lava	Muir Toll Burn	Campsie Fells	Craig 1980	
3	analcime trachybasalt	lava	Blaikie Heugh	E. Lothian	Sum Progr 1905	G335
4	analcime trachyandesite	lava	Halket	Lugton	Sum Progr 1923	G164
5	phonolitic trachyte	lava	Winkingfield	Darvel	Guppy et al 1931	G95
6	phonolitic trachyte	plug	Bass Rock	E Lothian	Hatch 1892	G98
7	phonolitic trachyte	plug	N Berwick Law	E Lothian	Hatch 1892	G95
8	phonolite	laccolith	Traprain Law	E Lothian	Hatch 1892	G107
9	phonolite	laccolith	Traprain Law	E Lothian	Sum Progr 1922	G106
10	phonolite	intrusion	Fintry	Strath Blane	Sum Progr 1907	G104
11	phonolitic trachyte	plug	Townhead of Grange	Lugton	Sum Progr 1923	G103
12	phonolitic trachyte	intrusion	Underlaw	Darvel	Sum Progr 1926	G105
13	analcime trachyandesite	plug, margin	Loudoun Hill	Darvel	Guppy et al 1931	G164
14	analcime trachyandesite	plug, centre	Loudoun Hill	Darvel	Guppy et al 1931	G165

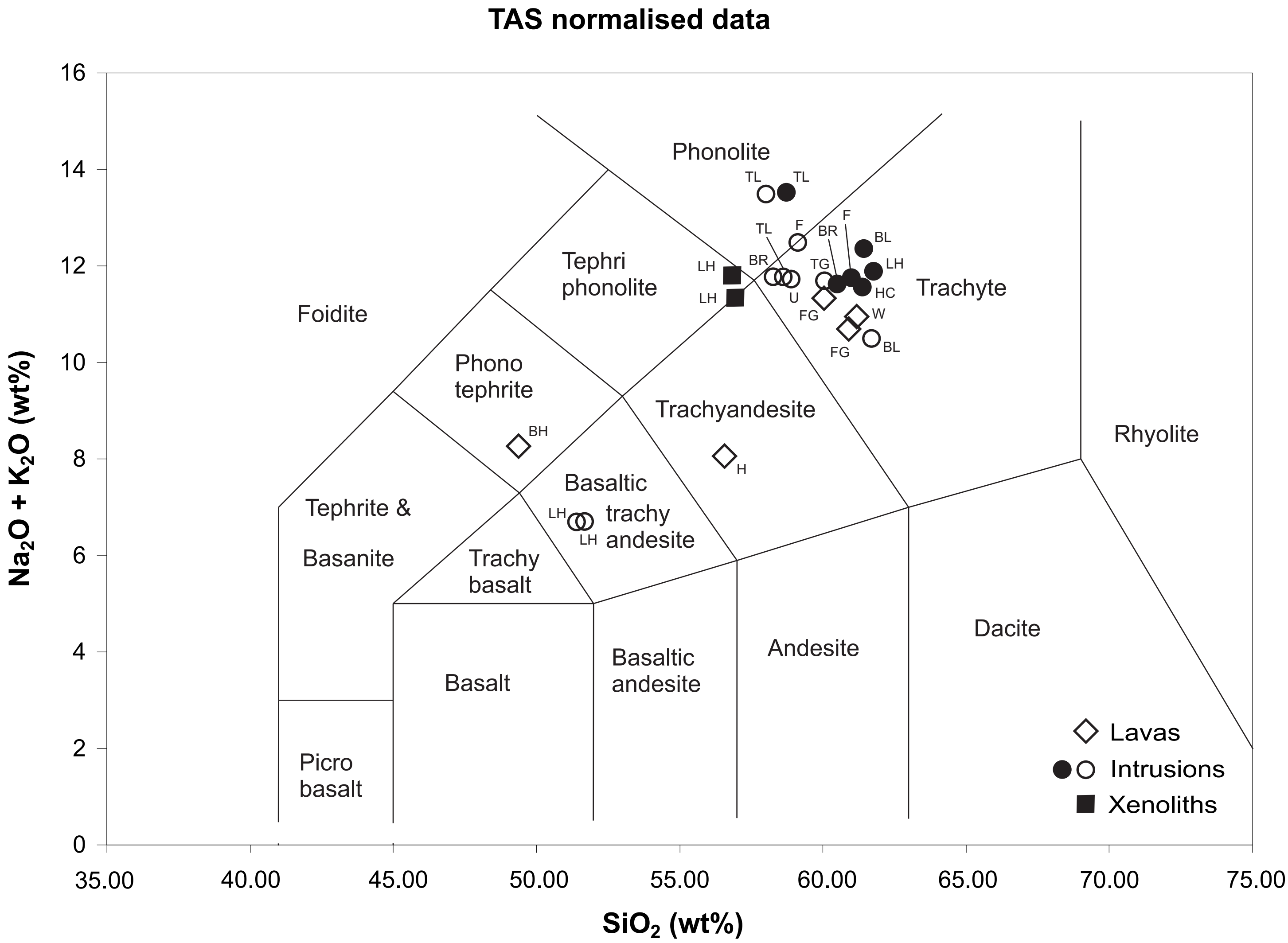
Dates of first publication are given; most have appeared in subsequent publications; in particular, all except 1 & 2 are included in Guppy et al., 1931 with the reference numbers shown e.g. G103.

Sum Progr = *Summary of Progress of the geological Survey of Great Britain and Museum of Practical geology for the year* …...

Table 1 Evolved, silica-undersaturated volcanic and intrusive rocks of Carboniferous to Permian age in central and southern Scotland

Name	Location	BGS sheet	Grid Ref	Form	Lithologies	Key references	Anals
North Berwick	E. Lothian	33W	NT 555 857	lava	analcime trachybasalt	Bennett,1945; Martin, 1955; McAdam & Tulloch, 1985	
Blaikie Heugh	E. Lothian	33E	NT 579 731	lava	analcime trachybasalt	Bennett, 1945; McAdam & Tulloch, 1985	1
Fin Glen	Campsie Fells	30E	NS 608 807	lava	phonolitic trachyte	Craig, 1980; MacDonald & Whyte, 1981	2
Halket	Lugton	22E	NS 423 525	lava	analcime trachyandesite	Richey et al., 1930	1
Winkingfield	Darvel	22E, 23W	NS 607 383	lava	phonolitic trachyte	Phemister c. 1939, unpubl.	1
Bass Rock	E. Lothian	33E	NT 602 873	plug	phonolitic trachyte	McAdam & Tulloch, 1985	2
N Berwick Law	E. Lothian	33W	NT 557 842	plug	phonolitic trachyte	McAdam & Tulloch, 1985	2
Traprain Law	E. Lothian	33E	NT 582 747	laccolith	phonolite	MacGregor & Ennos, 1922; Bennett,1945; Tomkeieff, 1952; De Souza, 1974, 1979; McAdam & Tulloch, 1985; Williamson and Millward, 2003	3
Hairy Craig	E. Lothian	33E	NT 577 751	sheet	phonolite	McAdam & Tulloch. 1985	1
Fintry	Strath Blane	30E, 31W	NS 614 863	intrusion	phonolite	Clough et al., 1925	2
Townhead of Grange	Lugton	22E	NS 452 525	plug	phonolitic trachyte	Richey et al., 1930	1
Mearns	Newton Mearns	22E	NS 546 549	plug	phonolitic trachyte	Richey et al., 1930	
Underlaw	Darvel	22E	NS 590 390	intrusion	phonolitic trachyte	Richey et al., 1930	1
Laird's Seat	Darvel	22E	NS 601 457	plug	phonolitic trachyte	Richey et al., 1930	
Priestland	Darvel	22E	NS 582 377	intrusion	phonolitic trachyte	Richey et al., 1930	
Loudoun Hill	Darvel	23W	NS 608 379	plug	analcime trachyandesite phonolitic trachyte analcime-syenite	Phemister c. 1939, unpubl.	5
Skelfhill Pen	Teviothead	17W	NT 441 031	2 intrusions	phonolite	McRobert, 1920	
Millstone Edge	Teviothead	17W	NT 434 012	dykes	phonolitic trachyte		
Linhope Burn	Teviothead	17W	NT 413 011	dykes	phonolitic trachyte	McRobert, 1920	
Carewoodrig	Teviothead	17W	NY 421 992	plug	phonolitic trachyte	McRobert, 1920	
Pikethaw Hill	Teviothead	10E, 11W, 17W	NY 369 977	intrusion	phonolite	McRobert, 1920; Lumsden et al., 1967	


1000
100
10
1
REE/chondrite
La
Ce
Pr
Nd
Sm
Eu
Gd
Dy
Ho
Er
Yb
Lu
TR1
TR2
TR3
TR4
TR5
TR6
TR7
TR8



TAS normalised data
16
14
12
10
8
6
4
2
0
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
$Na_2O + K_2O$ (wt%)
SiO_2 (wt%)
Phonolite
Tephri phonolite
Foidite
Phono tephrite
Trachyandesite
Trachyte
Rhyolite
Tephrite &
Basanite
Basaltic trachy andesite
Trachy basalt
Basalt
Basaltic andesite
Andesite
Dacite
Picro basalt
TL
TL
TL
F
F
BR
BR
TG
BL
LH
HC
U
FG
W
FG
BL
LH
LH
BH
H
LH
LH
Lavas
Intrusions
Xenoliths