

SILICIC VOLCANISM IN THE RHENOHERCYNIAN ZONE: GEOCHEMISTRY AND TEMPORAL DEVELOPMENT

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Progressive Devonian rifting of continental crust in the Variscan Rhenohercynian Zone (RHZ) developed oceanic crust and an attenuated passive margin to the north. Accompanying mafic-silicic volcanism in these two sectors of the RHZ basin are chemically distinct. At the margins (in both SW England and the Rhenish Massif) the volume and chemical characterisation of silicic volcanism changes with time, together with the proportion of associated basaltic products.

In general, basin margin silicics are largely quartz-alkali feldspar \pm biotite-phyric, vitreous rhyolites and dacites, together with trachytes of peralkaline character. All silicics have within-plate, A-type granitoid chemical compositions. The Lower Devonian high/medium K calc-alkaline rhyolites exhibit high normalized values of Th and a negative Nb-Ta anomaly indicative of the involvement of continental crust and/or sediment in their generation. The Middle and Upper Devonian peralkaline trachytes have a much greater range of HFS element abundances, lack a crust component and have a more alkaline composition overall.

The observed temporal chemical changes are correlated to the degree of crustal attenuation at the basin margins during progressive lifting. Early initial rifting (together with an additional mantle heat source) was sufficient to induce partial melting of the continental crust with the production of the Lower Devonian calc-alkali rhyolites. By the time oceanic crust had developed in the axial zone, the margins were invaded by large volumes of alkali basalts that underwent extreme fractionation with the production of trachyte differentiates throughout the Middle and Upper Devonian.

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INTRODUCTION

The Variscan geology of Europe is classically divided into a number of tectonic zones (Kossmat, 1927) of which the northernmost external segment is the Rhenohercynian Zone (RHZ). Unlike those zones to the south the Upper Palaeozoic extensional basin of the RHZ has a brief history, developing in the earliest Devonian and closing by northward directed transpression during late Devonian through to mid-Carboniferous (Franke, 1989). Structural and stratigraphic correlation between different segments of the RHZ is well-documented, especially between SW England and the Rhenish Massif of northern Germany (e.g. Franke and Engel, 1982; Holder and Leveridge, 1986), although whether the RHZ as a whole reflects a continuous basin or a number of separate pull-apart basins is open to question (e.g. Barnes and Andrews, 1986).

One common feature of the RHZ in the SW England and German segments is the occurrence of extensive Devonian-Carboniferous syn-extensional bimodal volcanism. Within the volcanic suite, basalts (largely pillow lavas) and dolerites (high level sills) are dominant, whereas the more silicic components are relatively minor and much less well known. Mafic volcanic products are associated with both the rifted passive margin of the RHZ basin and the spreading axial zone with the development of alkalic within-plate basalts and mid-ocean ridge-type basalts respectively (Floyd, 1995).

This paper is concerned with the petrogenesis of the associated small-volume silicic volcanics situation on the passive margin of the basin in the SW England and German segments of the RHZ. The recognition that many of these volcanics are representative of the earliest expression of Variscan magmatism is important in understanding the association of volcanism and rifting in the progressive generation of the RHZ basin. Initially, Lower Devonian silicic volcanics are chemically characterised from the two segments, then compared with their analogues in the Middle and Upper Devonian to ascertain any temporal changes with progressive rifting.

ROCK TYPES AND LOCATION

In the early literature many of these rocks were given descriptive field terms, such as "felsite" or various types of "keratophyre", largely on account of their highly altered, fine-grained, siliceous and/or feldspathic character (e.g. Ussher, 1912; Flick, 1978, 1979). However, based on relict textures, primary phenocryst assemblages and geochemical data, most can now be directly compared with rhyolitic and trachytic types, that is, volcanic rocks of broadly acid composition (Jones, 1995). Because of the paucity of outcrop and good field relationships, as well as the often high degree of secondary alteration and deformation, it is not always possible to determine the original emplacement nature of the volcanics (intrusive or extrusive; lava or tuff). This is certainly true of some of the SW England localities (cf. Durrance, 1985), although silicic volcanics are more abundant and better exposed in Germany.

Minor silicic rocks occur in the Lower Devonian of SW England (near Modbury, S Devon, Fig.1) and the Rhenish Massif of northern Germany (Kirchhunden-Hilchenbach region, Fig.1). A representative selection of samples were collected from these regions for geochemical analysis; location details are given by Jones (1995). In general, there is a far greater abundance of better exposed Lower Devonian silicic volcanics in the Rhenish Massif than in S Devon, as well as further good occurrences throughout the Middle and Upper Devonian. However, to provide a suitable range of samples for analysis, field and stream cobbles were also collected from both regions in the vicinity of actual outcrops. Both thin section and chemical analysis confirmed compatibility between samples collected from known outcrops and nearby erosional debris.

Apart from the early mapping work of Ussher (1912), Durrance (1985) described the petrography of silicic rocks from the S Devon outcrops and recognized them as altered and recrystallized rhyolites that pre-dated cleavage development. On the basis of limited geochemical analyses (8 samples) they were distinguished from the

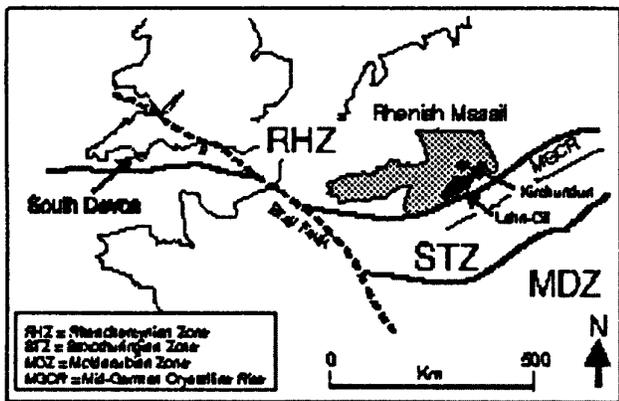


Figure 1. Relative location of Devonian silicic volcanics in SW England (S Devon) and the Rhenish Massif (Kirchundun) within the Rhehercynian Zone of the Variscan orogen.

Variscan granites and Permian rhyolites, and said to have been formed in an active margin environment. Work by the BGS Mineral Reconnaissance unit drilled 6 boreholes around the Whympston Wood outcrop (O.S. map 202; SX664503) in early 1987 and penetrated sheet-like intrusive bodies of rhyolite and dacite (Leake et al., 1988). A number of fresh samples selected from Whympston boreholes 1 (dacite) and 6 (rhyolite) were reanalysed by us and added to the S Devon surface outcrop database. Work on the Rhenish Massif silicic volcanics has been largely undertaken by Flick (1977, 1978, 1979, 1987) and, Flick and Nesbor (1988), although there are little chemical data (except major oxides) available. The above work has largely focussed on detailed petrography and rock classification based on an admixture of primary and secondary features. Many of the keratophyric types are recognized as altered alkali trachytes and rhyolites.

FIELD FEATURES

Due to the degraded nature of the S Devon quarries and outcrops it is difficult to determine the emplacement nature of many of the Lower Devonian silicic rocks (cf. Durrance, 1985). However, their massive appearance throughout, lack of flow banding and autobrecciation zones suggests that most are probably intrusive bodies. Similarly the Whympston borehole material lacks primary igneous features indicative of lava flows and are also considered to be intrusive sheet-like bodies that parallel the regional strike. The main outcrops and boreholes occur within the mudstone-dominated fluvial Dartmouth Beds of mainly Siegen age (Smith and Humphreys, 1991).

The Lower Devonian silicic volcanics in the Kirchhunden-Hilchenbach region of the Rhenish Massif show a range of emplacement situations within a marine environment, including: subaqueous flow-banded lavas (some showing ovoid pillow-like forms or "pods"), subaqueous lava domes (tholoids) with associated breccias, high-level intrusive lava domes, and intrusive sheet-like bodies. Both extrusive and intrusive varieties are closely associated in the field, although direct contact between the two (apart from faulted contact) has not been observed. Weathered out argillaceous xenoliths are sometimes a common feature of the subaqueous flows and the top parts of intrusive domes (Jones, 1995). Extrusive flows and domes are associated with shallow-marine slates and sandstones of Emsian age (Flick and Nesbor, 1988).

Middle and Upper Devonian silicic volcanics are also represented by both extrusive and intrusive analogues, but largely restricted to deep-water calcareous slates and sandstones of the Lahn-Dill synclines (Flick, 1978; 1979; Flick and Nesbor, 1988). Reworking of some of the subaqueous flows is indicated by the association of thin volcanoclastic debris flows packed with angular clasts of a similar composition. Unlike the Lower Devonian representatives, the lava

flows of the Middle and Upper Devonian do not contain any argillaceous xenoliths (Jones, 1995).

PETROGRAPHY

Due to subsequent Variscan deformation and metamorphism the volcanics often exhibit a strong textural and secondary mineral overprint, such that deduction of their primary features and compositions are dependant on relict textures and "immobile element" geochemical techniques. The mineralogical alteration of extrusive bodies was largely a consequence of post-eruption devitrification, with the development of spherulites and a "snow-flake" textured matrix of non-equilibrated quartz-feldspar grains. Both of these features are indicative of the originally glassy state of rapidly quenched subaqueous flows and domes. The subsequent effects of Variscan metamorphism were largely confined to granular recrystallization of the matrix (with equilibrium equigranular textures), together with variable growth of secondary K-feldspar (replacing albite), quartz and carbonate. Secondary silification, together with alkali metasomatism, were important processes that may have taken place soon after devitrification, as well as in response to Variscan metamorphism. Major textural overprint is seen in small shears with the development of brecciated to micromylonitic fabrics and the growth of associated secondary phyllosilicates.

The Lower Devonian extrusive volcanics of S Devon and the Rhenish Massif are largely quartz-feldspar-biotite-phyric glassy rhyolites and dacites, with spherulitic and microgranular (felsitic) textures (Durrance, 1985; Jones, 1995). Spherulites often nucleate on embayed and magmatically corroded quartz phenocrysts. The spherulites are of the sheaf-type (terminology of Lofgren, 1970) and on the basis that their morphology is related to temperature of formation (Lofgren, 1971), the rhyolite spherulites represent devitrification temperatures of between 550-600°C (Jones, 1995). Intrusive domes from the Rhenish Massif largely differ petrographically from the lava flows in that they are especially phenocryst-rich and at first sight in the field appear to have a microgranitic texture of quartz and feldspars, with little fine-grained matrix visible.

Middle and Upper Devonian silicic volcanics from the Rhenish Massif are largely quartz-feldspar-phyric trachytes with recrystallized, fine-grained "felsic" matrices. Variable replacement of albite phenocrysts by cryptoperthitic K-feldspar again testifies to extensive post-consolidation alkali metasomatism.

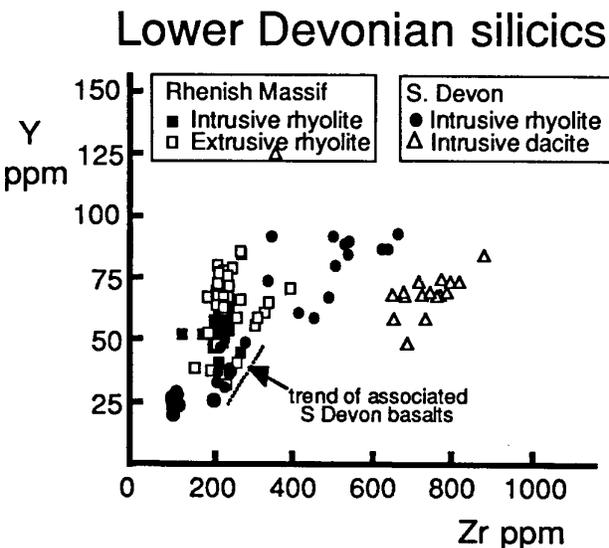


Figure 2. Development of different chemical suites of Lower Devonian rhyolites and dacites within sectors of the RHZ in terms of variable Zr/Y ratios.

Textural variations are seen in the marginal zones of silicic lava "pods" which are fragmentary in appearance and crowded with quenched shallow-tail albite microliter. These zones represent the spalled fragments of chilled margin around the lava "pods" (cf. De Rosen-Spence *et al.*, 1980).

GEOCHEMISTRY

Representative Devonian silicic volcanics from both S Devon and the Rhenish Massif were chemically analysed by XRF spectrometry (Jones, 1995); methods, precision and accuracy are given by Floyd and Castillo (1992).

Classification and alteration effects

Silicic volcanics are susceptible to chemical changes due to glass hydration and post-consolidation alteration (Scott, 1971; Weaver *et al.*, 1990). The majority of the Lower Devonian silicics have elemental abundances that indicate they have undergone hydrothermal alteration, including secondary silification and LIL element (especially Na and K) metasomatism, similar to other ancient rhyolites (e.g. Maclean and Hoy, 1991). However, using stable ratios of incompatible elements, such as, Zr/TiO₂ and Nb/Y (Winchester and Floyd, 1977), and Zr-Nb relationships (Leat *et al.*, 1986) the Lower Devonian silicics are confirmed as medium/high-K calc-alkaline rhyolites and rhyodacites, as suggested by the relict petrography. The field-designated dacites (from Whympston borehole 1, S Devon), which have the highest Zr contents (>650 ppm), are more peralkaline in character. In contrast, and in line with their petrographic classification, the Middle and Upper Devonian silicics are chemically classified as peralkaline trachytes.

Characteristic chemical features

Lower Devonian rhyolites and dacites have a number of distinctive chemical features: (a) They define a number of distinct trends with variable Zr/Y ratios (Fig.2) that may reflect different partial melt batches. Intrusive and extrusive rhyolites from the Rhenish Massif define the same trend, suggesting that they are chemically related, but are clearly different to the intrusive rhyolites and dacites of S Devon. (b) Ocean Ridge Granite-normalized incompatible element patterns typically exhibit Nb-Ta negative anomalies and flat HFS values (Fig.3). (c) Normalized REE patterns show light REE enrichment with Eu anomalies ($Eu/Eu^* = 0.3-0.5$). (d) They have high, and very variable, stable LIL/HFS element ratios (e.g. Ce/Zr, Th/Nb). In general, the Lower Devonian rhyolites and dacites have chemical features characteristic of within-plate A-type (anorogenic) granitoids (as defined by the chemical discriminators of Pearce *et al.*, 1984; Whalen *et al.*, 1987; Eby, 1990).

Middle and Upper Devonian peralkaline trachytes (Rhenish Massif) also exhibit a number of chemical suites (in terms of variable Zr/Nb ratios), but all normalized patterns are characterized by strong light REE enrichment and negative Eu anomalies, but lack any Nb-Ta depletion (Jones, 1995). Chemical discrimination indicates they also have within-plate A-type granitoid compositions.

PETROGENESIS

The different chemical groups represented by the Lower Devonian rhyolites and dacites indicate that they are not simply related by closed system fractionation, but probably represent different partial melts or sources. However, some of the variation within each chemical group is largely the consequence of feldspar fractionation as shown by parallel REE patterns and the progressive development of Eu anomalies in more silicic varieties. Extreme fractionation of the associated Lower Devonian basalts (S Devon) could account for the production of some of the rhyolites (Fig.2), although this is considered unlikely in view of the extensive range of stable LIL/HFS ratios displayed that cannot be generated by either

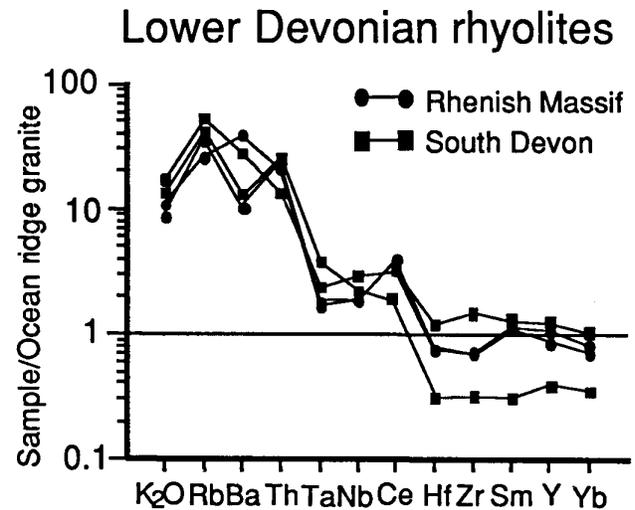


Figure 3. ORG-normalized multi-element diagram showing the chemical similarity between Lower Devonian rhyolites from S Devon and the Rhenish Massif. Note the present of a negative Nb-Ta anomaly. Normalization factors after Pearce *et al.* (1984).

closed system fractionation or assimilation with fractional crystallization (AFC) processes. Instead, modelling suggests that the partial melting of heterogeneous continental crust with the variable assimilation of greywacke and mudstone, or possibly the direct melting of sediment compositions, could produce the high LIL/HFS ratios observed (Jones, 1995). A strong crustal presence, especially the involvement of sediments, in the petrogenesis of the Lower Devonian rhyolites is supported petrographically by the presence of numerous sediment fragments that could represent source restite. Further chemical evidence is provided by the characteristic presence of Nb-Ta negative anomalies in normalized spidergrams (Fig.3) - a feature which is generally considered indicative of crustal involvement.

Middle and Upper Devonian trachyte chemical groups have their equivalents among the associated basalts and dolerites which are also alkaline in character. Continuous incompatible element trends between the lithologies suggests that mafic and later feldspar fractionation of the basalts have produced the trachytes (Jones, 1995).

TEMPORAL DEVELOPMENT OF VOLCANISM

There are significant differences in the nature of the RHZ basin margin volcanics with time from the Lower Devonian to the Middle and Upper Devonian. The Lower Devonian silicics are mainly calc-alkaline rhyolites and dacites derived by partial melting of continental materials and/or sediments, whereas the Middle/Upper Devonian silicics are peralkaline trachytes derived by extreme fractional crystallization of associated basalts, with no involvement of continental crust (Fig.4). Although both temporal groups are typical of within-plate A-type granitoids, the Lower Devonian silicics are representative of the A2 subgroup, whereas the Middle/Upper Devonian silicics belong to the A1 subgroup (subgroups as defined by Eby, 1992). The subgroups are also a reflection of genesis (Eby, 1992), with the A1 subgroup being largely basic fractionates, and the A2 subgroup being mainly derived by crustal melting; both origins being supported by our RHZ data (Fig.4).

The temporal chemical change in the silicics also has its equivalent in the associated basalts. The earliest Lower Devonian basalts of S Devon and the Rhenish Massif are mainly tholeiites variably contaminated by continental crust, whereas the later Devonian marginal basalts and dolerites are almost exclusively alkali basalts (Floyd, 1995; and unpublished data).

We consider that the chemical affinities of bimodal volcanism throughout the Devonian can be related to the progressive development

of rifting in the RHZ. The sedimentary record of the RHZ reflects a period of early Devonian to Lower Carboniferous crustal extension and subsidence (Franke and Engel, 1982) with the eventual development of ocean lithosphere in the axial zone. Throughout the Devonian the progressive attenuation of the continental crust is reflected in the increase in rifting of the margins as well as the development of oceanic crust in the axial portion of the RHZ basin. In the Lower Devonian crustal attenuation was relatively minor with low stretching factors ($\beta < 2$) and limited penetration of magmatic material. At this stage small volume tholeiitic basalts were contaminated by the surrounding voluminous continental crust. An uprising mantle source would provide the extra heat necessary for partial melting of the crust and the generation of the Lower Devonian A2-type calc-alkali rhyolites. Further crustal attenuation ($\beta > 2$) in the marginal zone would allow ascending mantle sources to undergo increased melting with the production of large volumes of basaltic melts. These melts probably ponded in the lower crust and via fractionation developed more intermediate/acid components - the Middle/Upper Devonian A1-type trachytes.

In most crustal rifting models the extension of the lithosphere results in the decompression of the underlying asthenosphere, a conductive rise in the geothermal gradient and diapiric injection of hot asthenosphere into the base of the lithosphere (e.g. McKenzie and Bickle, 1988). Syn-extensional melts will be derived from both the partial melting of the asthenosphere and the attenuated

continental crust, the former of which may be contaminated with or have a high crustal component (e.g. Leeman and Fitton, 1989). These general conditions appear to fit the progressive development of RHZ volcanic history.

CONCLUSIONS

1. Syn-extensional intrusive and extrusive silicic rocks are some of the first expressions of the extensive bimodal volcanism in the SW England and Rhenish Massif segments of the RHZ. The silicic volcanics of these two sectors are broadly similar in chemical and petrographic composition.

2. The Lower Devonian of S Devon is dominated by intrusive medium/high-K calc-alkali rhyolites and dacites that comprise a number of chemical suites. The Rhenish Massif exhibits comagmatic extrusive flows (some tholoids) and intrusive domes of similar calc-alkali rhyolites. The silicic volcanics are largely unrelated chemically to the associated minor basalts and were generated by the partial melting of continental crust and/or greywacke-type sediments.

3. The Middle and Upper Devonian in the Rhenish Massif shows the development of various peralkaline trachyte suites that represent the differentiation products of the associated alkali basalts.

4. All Devonian silicic volcanics have typical within-plate and A-type granitoid chemistry consistent with magmatism associated with rifted passive margins. In terms of anorogenic granite subgroups, the Lower Devonian silicics are A2-types, whereas the Middle/Upper Devonian are A1-types. The former group are distinctive in exhibiting a strong crustal influence in their genesis.

5. The change in chemistry and mode of origin from calcalkaline to peralkaline silicics with time is related to the progressive development of rifting in the margins of the RHZ basin. At low degrees of rifting ($\beta < 2$) melting of attenuated continental crust produced the calc-alkali rhyolites, whereas later, more extensive rifting ($\beta > 2$) produced large volumes of basalt that underwent fractionation to trachyte end-products.

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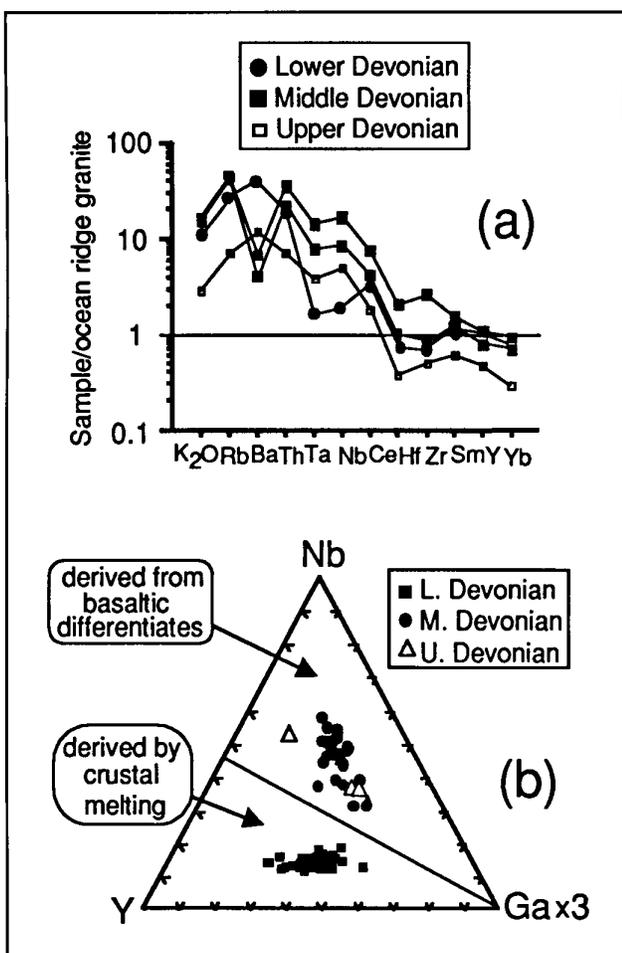


Figure 4. Diagrams illustrating chemical differences between Lower Devonian rhyolites and Middle/Upper Devonian trachytes. (a) ORG-normalized multi-element plot showing the presence and absence of a Nb-Ta anomaly, (b) Discrimination between A1 (derived by differentiation) and A2 types (derived by crustal melting) of anorogenic granitoids (diagram from Eby, 1992).

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