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Isotopic and geochemical investigation of a carbonatite-syenite-phonolite diatreme, West Eifel (Germany)

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ABSTRACT

The Rockeskyll complex in the north, central part of the Quaternary West Eifel volcanic field encapsulates an association of carbonatite, nephelinite and phonolite. The volcanic complex is dominated by three eruptive centres, which are distinct in their magma chemistry and their mode of emplacement. The Auf Dickel diatreme forms one centre and has erupted the only known carbonatite in the West Eifel, along with a broad range of alkaline rock types. Extrusive carbonatitic volcanism is represented by spheroidal autoliths, which preserve an equilibrium assemblage. The diatreme has also erupted xenoliths of calcite-bearing feldspathoidal syenite, phonolite and sanidine and clinopyroxene megacrysts, which are interpreted as fragments of a sub-volcanic complex. The carbonate phase of volcanism has several manifestations; extrusive lapilli, recrystallized ashes and calcite-bearing syenites, fragmented during diatreme emplacement.

A petrogenetic link between carbonatites and alkali mafic magmas is confirmed from Sr and Nd isotope systematics, and an upper mantle origin for the felsic rocks is suggested. The chemistry and mineralogy of mantle xenoliths erupted throughout the West Eifel indicate enrichment in those elements incompatible in the mantle. In addition, the evidence from trace element signatures and melts trapped as glasses support interaction between depleted mantle and small volume carbonate and felsic melts. This close association between carbonate and felsic melts in the mantle is mirrored in the surface eruptives of Auf Dickel and at numerous alkaline-carbonatite provinces worldwide.

Keywords: carbonatite, syenite, phonolite, stable isotopes, radiogenic isotopes.

Introduction

The occurrence of carbonatitic and felsic rock types at Rockeskyll is unique in the dominantly alkali-mafic West Eifel volcanic field. The felsic and carbonatitic rocks are linked to a single diatreme vent, which was emplaced adjacent to an alkali-mafic maar volcano and a nephelinitic stratacone. The diatreme erupted extrusive carbonatitic lapilli and ash, and carried a wide range of felsic (syenite, phonolite, sanidine) xenoliths to the surface. The extrusive carbonatite has been described elsewhere (Riley *et al.*, 1996) but here, the syenite, phonolite, sanidine and carbonate ashes are discussed. The stable (C and O) and radiogenic (Sr and Nd) isotope systematics of all the diatreme eruptives are presented and their pre- and post-magmatic history is analysed. The association between carbonate, felsic and alkali-mafic rock types are discussed in the context of mantle metasomatism models.

Geological setting

The Quaternary volcanic province of the West Eifel covers an area of *c.* 600 km^2, was active from *c.* 0.6–0.01 Ma and erupted 1.7 km^3 of magma (Mertes and Schmincke, 1985). The province, which comprises some 250 eruptive centres (Fig. 1), is dominated by alkaline (sodi-potassic)

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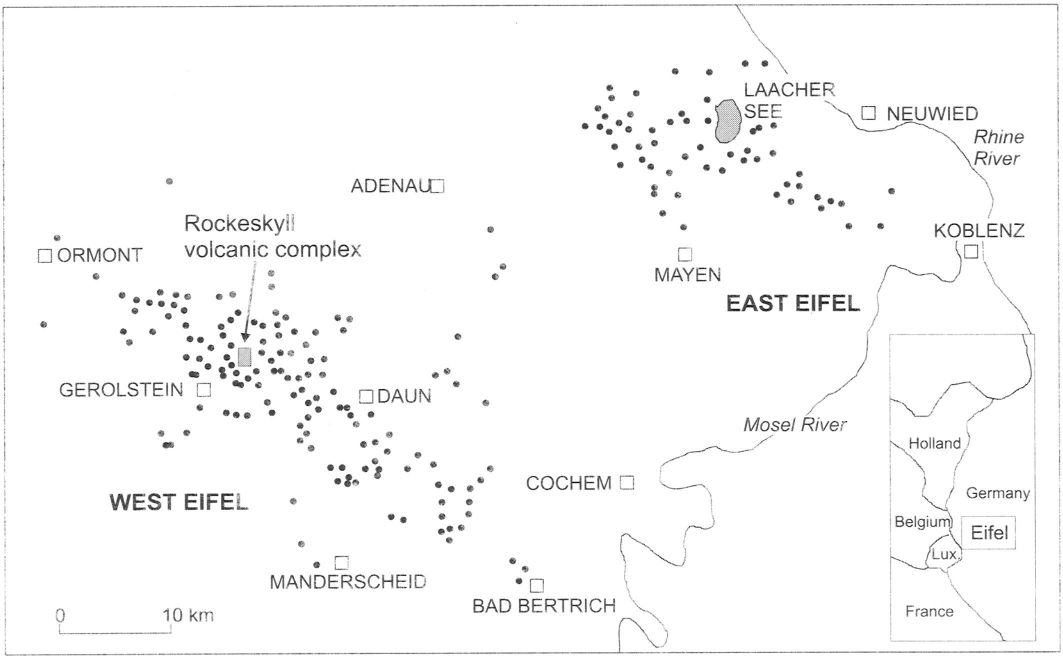


FIG. 1. Distribution of eruptive centres of Quaternary West and East Eifel volcanic fields (Mertes and Schmincke, 1983).

mafic magmatism, occurring as maar eruptives, scoria cones, lava flows and pyroclastic vents.

The Rockeskyll complex is located some 5 km northeast of Gerolstein (Fig. 1) and 1 km west of Rockeskyll village. It comprises several overlapping volcanic centres, which erupted a broad range of alkaline, and carbonatite rock types, dated at *c.* 0.5 ± 0.1 Ma (Mertes and Schmincke, 1983). Hopmann (1914) first commented on the unique occurrence of felsic rock types at Rockeskyll and drew similarities to the Laacher See in the East Eifel. Parallels were drawn after finding syenite, phonolite and sanidine fragments in the tuffs and soils near Rockeskyll. Hopmann (1914) also commented on the existence of calcite within the syenites, but included no description of carbonatite from the same vent. The first report of carbonatite from Rockeskyll, and from the West Eifel was made by Lloyd and Bailey (1969), who described the petrography and trace element geochemistry of two carbonate-rich fragments from the tuffs near Rockeskyll, and confirmed their magmatic origin. Riley *et al.* (1996) have reported the presence of carbonatitic autoliths from the same vent, indicating a new facet of carbonatitic activity at Rockeskyll.

Haardt (1914) first described the alkali-mafic deposits at Rockeskyll and documented an uppermost melilite nephelinite lava, earlier leucite-bearing lavas and also included a description of the nearby, sanidine-bearing tuffs. Three distinctive volcanic centres have been identified at Rockeskyll, depicted in the magnetic anomaly map of the region (Fig. 2); the maar crater to the southeast of Lammersdorf village (centre 1), Kyllerkopf hill alkali-mafic scoria cone (centre 2) and the carbonatite-syenite diatreme at Auf Dickel (centre 3).

Southeast Lammersdorf maar deposits (centre 1)

The centre is a remnant maar crater, demarcated by a pronounced positive anomaly (Fig. 2), some 600 m in diameter, although the maar itself may well have been up to three times this diameter. Quarry exposures reveal up to 45 m of maar pyroclastic rocks, which are well sorted, normally graded and contain a high percentage of pulverized country rock tephra, accompanied by alkali-mafic scoria, xenocrysts of clinopyroxene and phlogopite, and fragments of peridotite. Peridotite xenoliths in the pyroclastic pile are

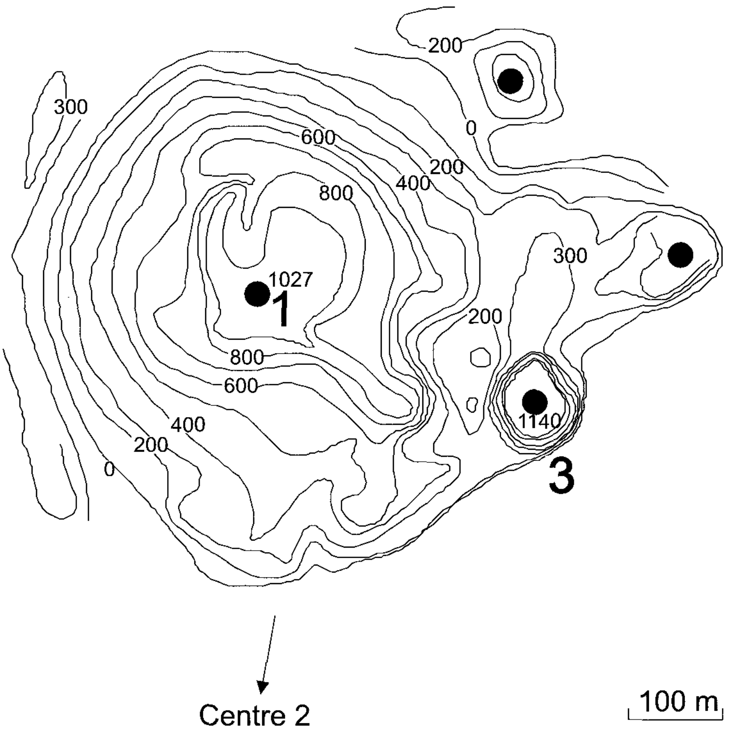


FIG. 2. Magnetic anomaly map and volcanic centres of the Rockeskyll complex (Mertes, 1982).

typically lherzolite fragments, which occasionally have jackets of mica-clinopyroxenite.

Kyllerkopf strombolian deposits (centre 2)

The Kyllerkopf volcanic centre, in the south of the complex, preserves a central alkali-mafic lava spine and proximal scoria deposits. The scoria are steeply dipping, exhibit a large range in clast size and are strongly reddened as a result of steam oxidation near the vent. The lavas and pyroclastic rocks are all alkali-mafic in composition, ranging from olivine nephelinite and leucite nephelinite to melilite nephelinite.

Auf Dickel diatreme (centre 3)

Carbonatite-syenite magmatism is restricted to Auf Dickel, where 10–15 m deep cuttings expose a partly eroded diatreme, which cuts through earlier bedded, but reworked pyroclastic rocks. A diatreme facies is suggested by the nature of the erupted products and by existing magnetic data (Mertes, 1982) which clearly shows a positive magnetic high of 1140 nT near the site of the present exposures (Fig. 2). The tuffisite ash of the diatreme, which hosts the erupted material is largely unbedded, although slump structures are in evidence near the centre of the deposit. Similar features have, however, been considered a primary characteristic of tuffisite pipes (e.g. Schwabian field, southern Germany; Cloos, 1941) where they are a result of fluidized emplacement.

The diatreme is host to a wide range of alkaline and carbonate-rich rock types; xenoliths of calcite-bearing, feldspathoidal syenite, phonolite and megacrysts of water-clear sanidine are present. Evidence for extrusive carbonatite is provided by spheroidal cored lapilli that vary in size from 1–4 cm and are considered to be autoliths, as they are cognate with the host, carbonate-rich ash. Nucleated autoliths and spheroidal lapilli are common in carbonatite and silica-undersaturated diatreme eruptions, e.g. Urach (southern Germany), Keller *et al.* (1990); Rufunsa (Zambia), Bailey (1989) and Cupaello, Italy (Stoppa and Cundari, 1995). They are thought to represent juvenile melt material,

TABLE 1. Major element, trace element and isotopic data for erupted material from Auf Dickel diatreme

Sample: Rock type	AD1 carb.	AD2 carb.	AD4 carb.	RKK251 syenite	TRR21 syenite	FL363 syenite	FL365 syenite	FL366 syenite	FL370 syenite	FL380 syenite	KQS1 phon.	RKK69 phon.	RKK1 phon.	RKK17/9 ash	RKK17/7 ash	RKK85 ash	FL378 sanid.	RKK7 sanid.
SiO_2	13.3	15.8	16.1	50.49	53.27	53.24	54.66	50.76	58.4	48.24	56.3	54.03	55.35	50.92	40.43	33.93	64.69	64.75
Al_2O_3	7.38	5.45	6.58	17.66	18.87	18.41	20.96	17.53	20.32	16.54	20.14	20.37	20.41	12.15	8.79	8.51	18.69	19.35
TiO_2	1.16	0.75	0.98	0.22	0.26	0.27	0.38	0.52	0.19	0.28	0.25	0.36	0.24	1.63	1.47	0.72	–	–
Fe_2O_3*	6.11	5.49	5.47	3.3	3.87	4.03	3.53	5.33	2.72	3.7	3.08	3.45	3.13	10.62	10.08	9.2	0.23	0.19
MgO	0.9	1.91	1.12	0.41	0.53	0.59	0.37	0.83	0.08	0.13	0.32	0.58	0.29	4.74	6.3	2.19	0.01	0
CaO	39.1	38.9	38.1	5.78	3.44	3.23	1.6	5.93	0.72	9.67	2.3	3.77	2.38	11.31	19.29	21.63	0.12	0
Na_2O	2.8	1.92	2.02	6	6.24	5.69	3	2.83	6.93	3.77	5.7	4.73	5.69	0.7	0.44	0.37	3.12	3.09
K_2O	1.3	0.22	1.1	8.14	8.81	8.56	9.7	9.01	6.15	7.89	7.14	6.82	7.22	1.99	0.83	1.56	11.97	12.14
MnO	0.2	0.07	0.12	0.17	0.17	0.18	0.2	0.26	0.17	0.11	0.32	0.28	0.36	0.34	0.38	0.56	–	–
P_2O_5	2.55	2.34	2.21	0.37	0.26	0.24	0.11	0.05	0.23	0.16	0.16	0.33	0.14	1.31	0.63	0.42	–	–
LOI	22	22.4	22.3	5.32	3.73	3.38	3.52	6.05	2.56	9.26	3.66	4.9	4.38	4.47	11.06	20.87	–	–
Total	100.14	98.01	98.5	97.87	99.45	97.85	98.04	99.1	98.47	99.76	99.38	99.61	99.59	100.19	99.71	99.97	98.95	99.94
Ba	3580	4120	4080	2680	2312	2299	3896	2614	2099	3817	1959	2040	1676	1157	719	421	8392	8886
Cl	–	–	–	290	410	349	6	6	6	6	648	1243	753	155	196	118	6	40
Co	–	–	–	17	3	12	19	18	3	15	6	20	27	30	28	18	–	–
Cr	–	–	–	5	5	17	44	15	86	3	3	30	8	112	234	96	–	–
Cu	–	–	–	13	13	14	13	19	13	30	8	10	5	52	62	48	–	–
F	–	–	–	395	225	589	1031	1381	200	200	200	200	266	1109	776	961	–	–
Ga	–	–	–	22	28	27	23	22	34	20	32	35	37	20	13	14	–	–
Hf	–	–	–	13	13	11	3	3	10	3	9	10	11	7	7	4	–	–
Nb	–	–	–	568	1422	1446	96	66	1397	65	947	1004	1002	195	55	41	–	–
Ni	–	–	–	9	9	11	14	13	18	13	14	3	8	67	62	33	–	–
Pb	–	–	–	8	9	10	17	17	15	21	25	25	22	23	9	14	–	–
Rb	–	–	–	140	166	164	214	195	123	137	157	153	161	83	104	70	179	190
S	–	–	–	12168	13564	11591	3041	2307	6701	6389	6435	8756	8736	340	53	473	41	58
Sr	9630	10560	9990	1934	1653	1531	1027	2383	866	2366	1604	1758	1569	1012	888	458	1120	1050
Ta	–	–	–	13	26	31	3	2	34	2	31	39	38	8	0	5	–	–
Th	–	–	–	34	55	56	7	4	37	9	69	62	62	28	9	5	–	–
U	–	–	–	33	27	27	3	1	26	2	12	13	12	–	–	–	–	–
V	–	–	–	180	236	256	197	272	101	102	124	120	122	250	403	316	–	–
Y	–	–	–	27	14	13	32	39	12	29	24	31	30	44	23	21	–	–
Zn	–	–	–	74	90	91	95	113	31	23	152	185	164	121	60	66	–	–
Zr	–	–	–	2032	1222	1296	147	207	1365	234	1772	1673	1733	496	221	150	–	–
La	–	–	–	65.25	41.07	34.69	59.24	51.27	52.68	84.22	66.71	97.12	90.35	41.9	47.3	46.85	0.91	0.85

Table 1. *(contd.)*

Sample:	AD1	AD2	AD4	RKK251	TRR21	FL363	FL365	FL366	FL370	FL380	KQS1	RKK69	RKK1	RKK17/9	RKK17/7	RKK85	FL378	RKK75
Rock type	carb.	carb.	carb.	syenite	syenite	syenite	syenite	syenite	syenite	syenite	phon.	phon.	phon.	ash	ash	ash	sanid.	sanid.
Ce	–	–	–	118.47	90.2	77.64	111.97	96.82	97	125.7	124.58	199.28	176.44	69.49	79.15	72.10	1.43	1.56
Pr	–	–	–	12.5	9.39	8.07	12.38	10.63	9.74	11.77	13.64	19.1	14.87	27.33	9.42	8.52	0.2	0.18
Nd	–	–	–	41.03	29.32	24.6	41.42	32.54	30.59	37.42	40.73	68.21	64.47	96.67	34.99	30.97	0.7	0.78
Sm	–	–	–	5.57	4.6	3.7	6.34	5.96	3.73	4.76	6.17	8.02	2.55	14.5	5.45	4.24	0.37	0.4
Eu	–	–	–	2.28	1.33	1.11	2.93	2.12	1.57	2.65	1.88	2.12	1.77	4.2	1.76	1.32	0.68	0.75
Gd	–	–	–	4.65	3.32	2.57	5.52	5.05	3.39	4.97	4.59	5.65	4.98	13.01	5.20	4.60	0.12	0.1
Tb	–	–	–	0.59	0.43	0.43	0.78	0.79	0.41	0.65	0.74	1.01	0.84	1.53	0.64	0.58	0.02	0.01
Dy	–	–	–	2.7	2.04	1.76	3.84	4.72	1.81	3.12	3.79	4.56	4.02	7.16	3.05	2.75	0.09	0.04
Ho	–	–	–	0.51	0.39	0.31	0.77	0.97	0.34	0.67	0.73	0.87	0.78	1.31	0.54	0.63	0.02	0.02
Er	–	–	–	1.42	1.09	0.96	2.16	2.89	1.04	1.96	2.25	2.54	2.28	3.55	1.54	1.56	0.07	0.09
Tm	–	–	–	0.21	0.17	0.19	0.28	0.42	0.13	0.29	0.35	0.44	0.4	0.52	0.19	0.22	0.01	0.02
Yb	–	–	–	1.22	0.97	0.9	1.75	2.63	0.87	1.71	2.62	6.14	4.66	2.81	1.08	1.32	0.04	0.05
Lu	–	–	–	0.19	0.2	0.22	0.29	0.39	0.16	0.28	0.47	0.59	0.5	0.45	0.26	0.24	0.01	0.01
$^{87}Sr/^{86}Sr$	0.70408	0.70416	0.7044	0.70433	–	–	–	0.70457	–	0.70483	–	–	–	–	–	–	–	0.70434
$^{143}Nd/^{144}Nd$	0.51279	0.51273	0.51273	0.51263	–	–	–	–	–	–	–	–	–	–	–	–	–	0.51263
$\delta^{13}C$	−5.3	−5.1	−4.8	−4.4	−4.7	−4.8	−6.3	−6.4	−6.7	−6.3	–	–	–	−5.6	−7.3	−10.4	–	–
$\delta^{18}O$	14.4	11.1	11.7	10.6	12.0	13.3	10.8	9.8	11.4	9.7	–	–	–	15.3	24.4	24.4	–	–

$^{87}Sr/^{86}Sr$ ratios are reported relative to the Eimer and Amend standard value of 0.70800. $^{143}Nd/^{144}Nd$ results were monitored using a solution of JMS Nd_2O_3.

Uncertainties are given at the 2σ level.

LOI, loss on ignition. Rock types: carb., carbonatite; phon., phonolite; ash, carbonatite ash; sanid., sanidine megacryst.

* Total Fe reported as Fe_2O_3. Relative precision of the major element oxide analyses is *c.* 1% of determined value, with the exception of Na_2O, P_2O_5 and S, which are ±10%. Relative precision of the trace element results (ppm) is ±10%.

REE contents for carbonate ashes are for the carbonate fraction only (separated by 0.5 M acetic acid).

–, not analysed.

which has nucleated in the diatreme, and has been rounded following fluidization. Magmatic autoliths are also reported from kimberlitic diatremes (Ferguson *et al.*, 1973).

Alongside the magmatic xenoliths carried within the tuffisite ash are fragments of the cover rocks of the Rhenish Massif; Muschelkalk limestone, Bunter sandstone and Devonian mudstones.

Analytical methods

Samples for whole rock analysis were crushed using an agate tema mill, and glass discs and powder pellets were prepared and analysed by PW1400 X-ray fluorescence at the University of Nottingham according to the techniques outlined in Riley (1994). The rare earth elements (*REE*) were analysed at the University of Bristol using a VG Elemental ICP-MS Plasmaquad.

Stable isotope analyses were performed at Universitat Göttingen using a Finnigan MAT-251 triple collector mass spectrometer and values were calibrated to Vienna PeeDee Belemnite (VPDB) for C isotope ratios and Vienna Standard Mean Ocean Water (VSMOW) for O isotope ratios. Strontium isotope ratios were determined using a VG-336 mass spectrometer at the University of Bristol. Neodymium isotopes were performed at the University of Pretoria using a VG-354 double focusing mass spectrometer.

Auf Dickel diatreme erupted rocks

Carbonatite

The mineralogy, geochemistry and petrography of the Auf Dickel autoliths are fully documented in Riley *et al.* (1996), therefore only a summary is presented here.

The autoliths are dominated by calcite, with modal data (Riley *et al.*, 1996) indicating between 48 and 59%; classifying them as carbonatitic (Woolley and Kempe, 1989). The calcite is characterized by high contents of SrO (*c.* 1.5%) and BaO (*c.* 1%), diagnostic of primary, magmatic calcite (Hogarth, 1989). The mineral compositions are comparable to calcite from other extrusive carbonatites (e.g. Uyanah, Woolley *et al.*, 1991; Cupaello *et al.*, 1995). Coexisting mineral phases identified throughout the suite of carbonatitic autoliths include melilite, clinopyroxene, vishnevite, melanite, apatite, sanidine and magnetite. The whole rock analyses of three carbonatitic autoliths are given in Table 1, and exhibit compositional similarities to other extrusive carbonatites (Riley *et al.*, 1996).

Syenite

More than 100 rounded and fragmental calcite-bearing feldspathoidal syenite xenoliths have been recovered from the tuffisite ash of the diatreme. The syenites are mineralogically dominated by the major felsic phases of sanidine and vishnevite and are accompanied by the accessory phases of calcite, biotite, clinopyroxene, amphibole, apatite, titanite, pyrochlore and magnetite.

Several syenites have been selected for XRF and rare earth element (*REE*) analysis and the data are listed in Table 1. A considerable variation in chemistry reflects the mineralogical heterogeneity of the syenite xenoliths. Some samples contain up to 20% modal calcite (e.g. FL380), whilst others (e.g. FL370) are calcite-free. This suggests the diatreme sampled a heterogeneous, possibly zoned syenite body. The *REE* pattern of the syenites (Fig. 3*a*) are typified by light *REE* (*LREE*) enrichment, flat heavy *REE* (*HREE*) levels and a pronounced positive Eu anomaly (Eu*: 0.3–0.9). The variation in Eu* implies differing degrees of feldspar (sanidine) accumulation.

Phonolite

Rare xenoliths of grey-green, phonolite have also been recovered from the Auf Dickel diatreme ashes. The phonolites have an aphanitic, green groundmass, studded with 10–20% euhedral phenocrysts of sanidine, vishnevite and rare biotite, hence comparable to those compositions from the more abundant syenite population. The whole rock chemistry for three phonolites is presented in Table 1 and shows little variation in major or trace element chemistry. The level of Ba (1569–2525 ppm) is high, and is strongly partitioned into the sanidine, whilst the levels of S (6435–8756 ppm) and Cl (613–1243 ppm) are also high, being strongly partitioned into the vishnevite. Contents of the high field strength elements (HFSE) are also high (Zr *c.* 1700 ppm, Nb *c.* 1000 ppm) as is the case for the vishnevite syenites. Chemically and mineralogically, the phonolites are analagous to the vishnevite syenites: they are all peraluminous with (Na+K)/Al in the range 0.744–0.849.

The *REE* plot (Fig. 3*b*) indicates *LREE* enrichment and flat *HREE* patterns. The

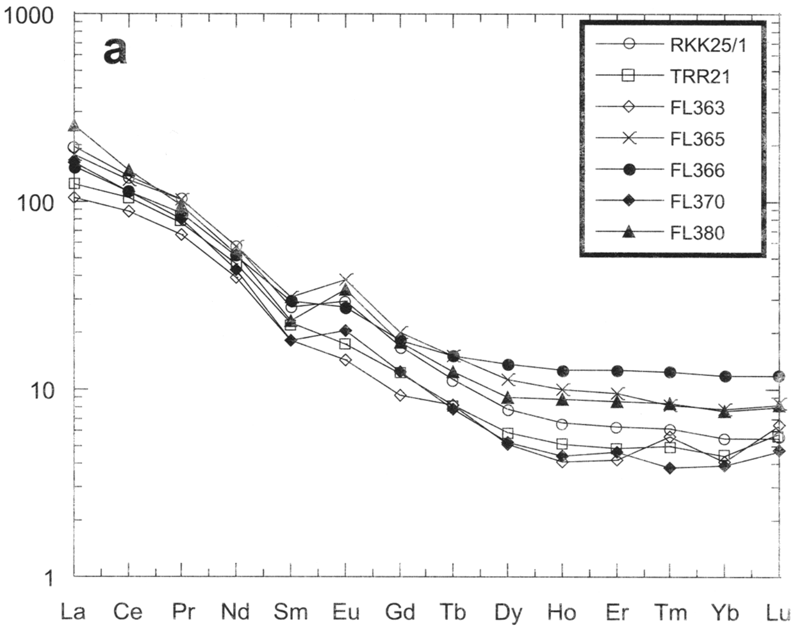


FIG. 3*a*. Chondrite normalized (Nakamura, 1974) *REE* plot for syenite xenoliths..

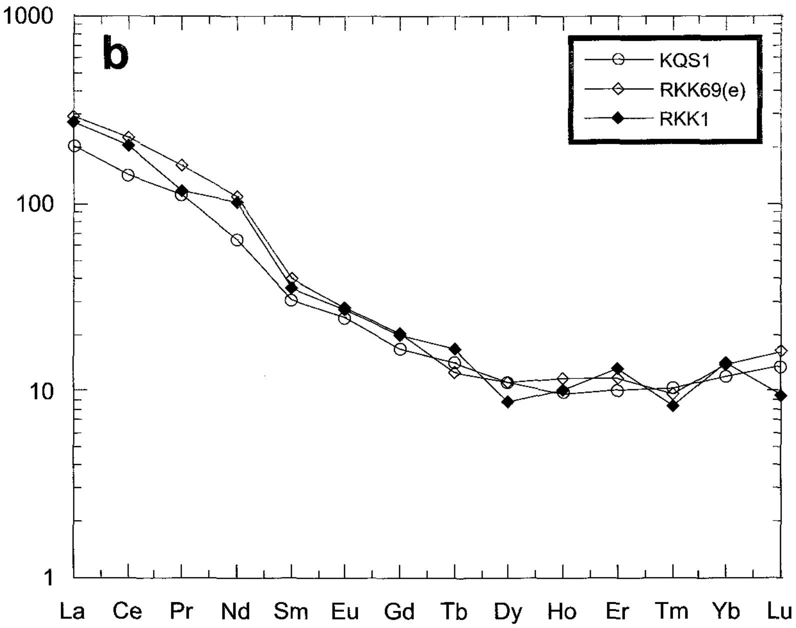


FIG. 3*b*. Chondrite normalized (Nakamura, 1974) *REE* plot for phonolite xenoliths.

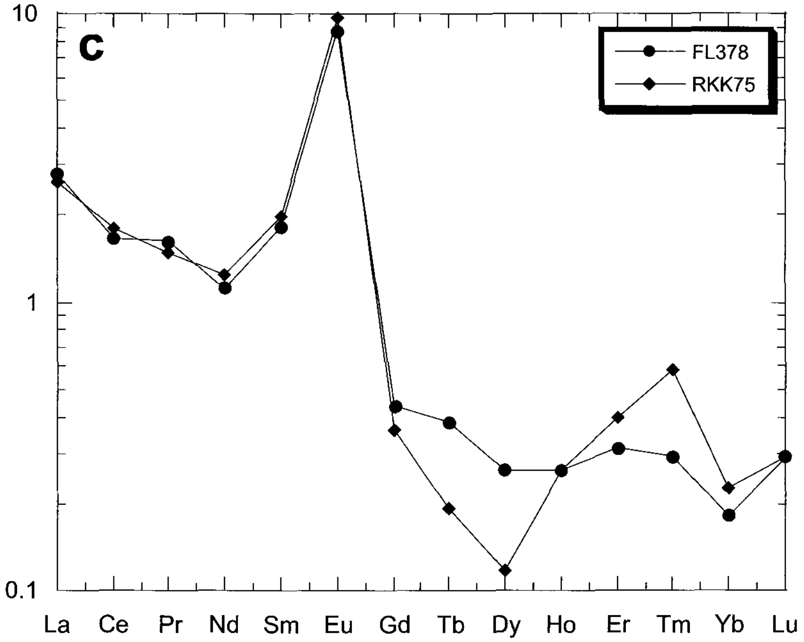
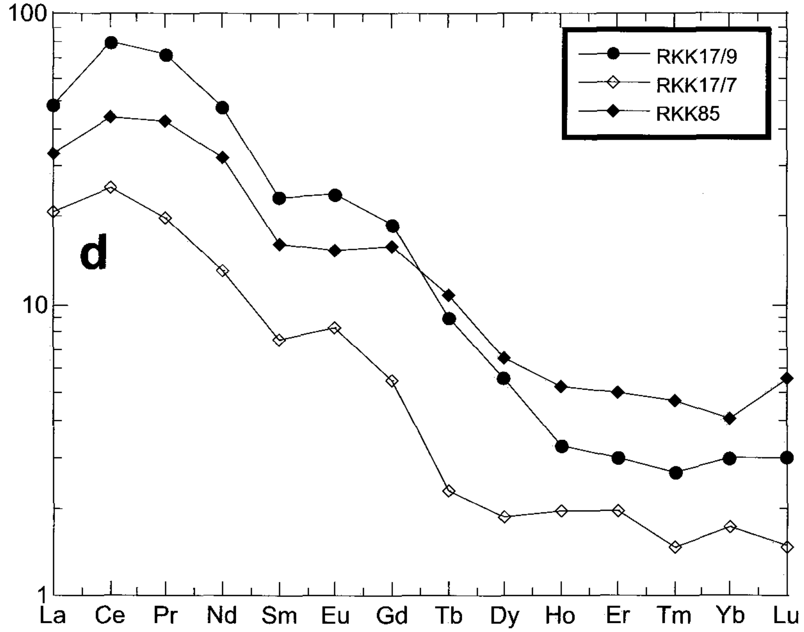


FIG. 3*c*. Chondrite normalized (Nakamura, 1974) *REE* plot for sanidine megacrysts.



. 3*d*. Chondrite normalized (Nakamura, 1974) *REE* plot for acid leached fraction from carbonate ashes.

phonolites compared to the syenites have similar *REE* patterns, but are more *LREE* enriched and have no Eu anomaly.

Sanidine megacryts

Water-clear sanidines are abundant in the fields surrounding the Auf Dickel diatreme, and have also been recovered from the tuffisite ash itself. The sanidines occur as fragmental crystals and vary in size from <1 cm in length, up to 6 cm, and are termed megacrysts. Two megacryst sanidines have been analysed by XRF and ICP-MS for their complete major and trace element composition. The data are presented in Table 1 and have near identical compositions to sanidine from the syenite and phonolite xenoliths. All of the sanidines have a composition in the range Or_{70-85}, and also a significant celsian ($BaAl_2Si_2O_8$; $Cn \approx 2$) component. The *REE* chemistry of two samples is plotted in Fig. 3*c* and characterized by a pronounced positive Eu anomaly, *LREE* enrichment and a flat *HREE* trend, with a slightly negative Yb anomaly.

Carbonate ashes

The tuffisite ash, which is host to the range of lithologies described previously, represents the pyroclastic equivalent of the carbonatite autoliths at Auf Dickel, and is also contaminated by a large proportion of xenocrystal material. Laminated ash horizons at the base of the unit (RKK85), and calcite-cemented lapilli tuffs (RKK17/7, RKK17/9) have been selected for analysis (Table 1). The laminar horizon, RKK85 is contaminated by less debris, and is richer in carbonate, indicated by acid leachate data (RKK85; 40% carbonate). Samples RKK17/7 (23% carbonate) and RKK17/9 (12% carbonate) are lapilli tuffs, which are stratigraphically higher in the unit and are cemented by calcium carbonate, with lapilli cored by clinopyroxene, biotite and country rock lithic fragments. To determine the *REE* constitution of the carbonate fraction in the laminated ashes and lapilli tuffs, dilute acid leachates (0.5 M acetic acid) were performed and the leachates analysed by ICP-MS (Table 1). The results are plotted in Fig. 3*d* and show an irregular *REE* pattern for the carbonate fraction, although all three samples are enriched in the *LREE* and have flat *HREE* patterns. Similar carbonate ashes and lapilli tuffs from Laetolil, Tanzania (Hay and O'Neil, 1983), Kaiserstuhl and the Urach, Germany (Keller *et al.*, 1990) are also interpreted to have undergone low temperature recrystallization, and sparry, low LILE calcite is preserved. At Auf Dickel, the implications are that the recrystallized, sparry calcite had magmatic origins, but the ash horizons were susceptible to re-equilibriation with water at low temperature.

Isotope geochemistry

Carbon and oxygen isotopes

The C and O isotope values of all carbonate-bearing rock types are presented in Table 1 and have been corrected to VPDB and VSMOW respectively and are expressed in delta notation. The results are plotted in Fig. 4 and exhibit a broad variation in both $\delta^{13}C$ and $\delta^{18}O$, which can be attributed to pre-, syn- and post-eruptive processes.

The carbonatitic autoliths and the syenite xenoliths plot close to, and within the field defined for primary igneous carbonatites (Taylor *et al.*, 1967), but trend towards more positive $\delta^{18}O$ and $\delta^{13}C$. The carbonate-bearing ashes sampled from the diatreme exhibit a marked spread away from the primary field toward the field for carbonate in weathering solutions of meteoric water. Two of the three analysed samples have high $\delta^{18}O$ values, and plot within the secondary field of Hay and O'Neil (1983), whilst the remaining sample (RKK17/9) plots midway between the primary and secondary fields. Limestone blocks from the tuffisite ash were also analysed to contrast with the magmatic carbonates and lie within the distinct field for marine limestones (Rollinson, 1993) at near zero $\delta^{13}C$ and positive $\delta^{18}O$ (+26 to 27‰).

A range of explanations are often applied to magmatic carbonates which plot away from the primitive magmatic field; these include heterogeneities in the source, isotopic exchange with isotopically different systems, fractionation between carbonate and a gaseous phase and truly secondary processes involving meteoric water.

The range in $\delta^{13}C$ and $\delta^{18}O$ in calcite from syenites is considered to be a function of fractionation between carbonate and a coexisting gas (CO_2-H_2O) phase. Fractionation in carbonatite complexes has been discussed elsewhere (e.g. Pineau *et al.*, 1973, Deines, 1989, Reid and Cooper, 1992) to explain the array of $\delta^{13}C$ and $\delta^{18}O$ ratios spreading from the field of primary carbonatites. It has been suggested that fractiona-

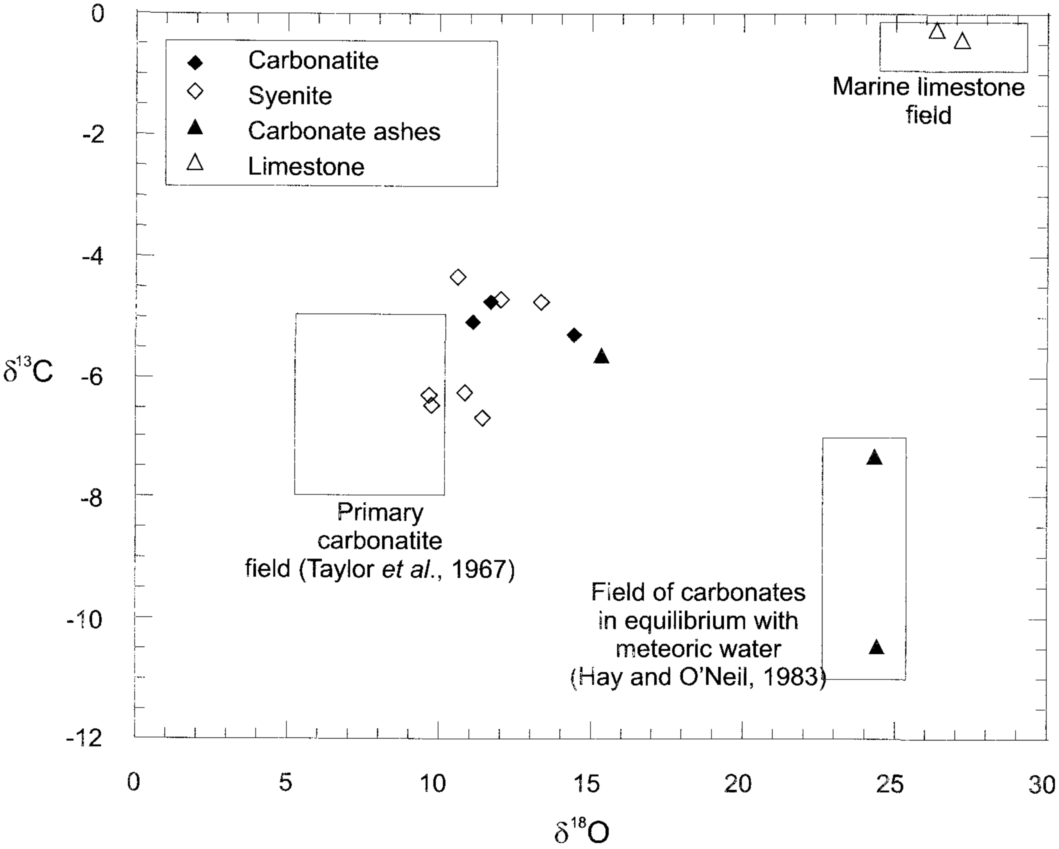


FIG. 4. Carbon and oxygen data for Auf Dickel xenoliths.

tion would be common in sub-volcanic complexes (Knudsen and Buchardt, 1991) and as such, may explain the isotopic variation within the feldspathoidal syenites, which were fragmented from a sub-volcanic massif at Rockeskyll.

The carbonatitic autoliths, which represent the extrusive phase of activity, have a similar isotopic signature to calcite from a sub-group syenite population, i.e. heavier $\delta^{13}C$ and $\delta^{18}O$, relative to the primary field of Taylor *et al.* (1967). The teardrop carbonatite lapilli of the Kaiserstuhl (Hubberten *et al.*, 1988) have a restricted isotopic range, with lighter $\delta^{13}C$ (−8‰) and heavier $\delta^{18}O$ (+15 to +17‰) relative to the primary intrusive field. Hubberten *et al.* (1988) considered that the lapilli may have undergone some isotopic shift with the lighter $\delta^{13}C$ being a function of heavier C partitioning into a coexisting CO_2 phase (Mattey *et al.*, 1990) and the heavier $\delta^{18}O$ a product of losing isotopically light water during eruption. These processes present few parallels with the Rockeskyll autoliths, which are isotopically distinct from the Kaiserstuhl lapillistones. This indicates that there was limited isotopic exchange with coexisting gas phases during the emplacement of the diatreme, but their isotopic evolution was restricted to sub-volcanic processes and may suggest that the Rockeskyll autoliths developed and crystallized within the neck of the diatreme and not sub-aerially.

Carbonate-bearing ashes and calcite-cemented, lapilli-tuffs were selected from different horizons in the exposed section of the diatreme. The samples, RKK17/7 and RKK85 are a calcite cemented lapilli tuff and a laminated ash horizon, respectively, from near the base of the diatreme and RKK17/9 is an unconsolidated, debris-rich ash from a higher stratigraphic level in the tuffisite. The ashes are plotted in Fig. 4, with two samples (RKK17/7 and RKK85) falling within the field defined by Hay and O'Neil (1983) in Fig. 4 for carbonate precipitated in weathering solutions of meteoric water. These two samples have near identical $\delta^{18}O$ values (*c.* +24‰) and indicate equilibration with meteoric water at low temperature. The $\delta^{13}C$ values are more negative than those of the primary intrusive field (RKK17/7, -7.33‰; RKK85, −10.44‰) and are also indicative of secondary carbonate (Hubberten *et al.*, 1988). The $\delta^{13}C$ (−5.65 ‰) and $\delta^{18}O$ (+15.31‰) of RKK17/9 are not characteristic of isotopic exchange between primary carbonate and meteoric water, but reflect post extrusive alteration processes, akin to extrusive natrocarbonatite from Oldoinyo Lengai (Keller and Hoefs, 1995). Similar isotopic signatures are also reported from the Kaiserstuhl (Hubberten *et al.*, 1988) where equilibrium with meteoric water has also been ruled out (Barker and Nixon, 1989) and the $\delta^{18}O$ signature has been attributed to the loss of light oxygen (^{16}O) just after eruption.

The two analysed limestone fragments were both collected as loose fragments from within the tuffisite ash itself. Both RKK86 and C26 are almost pure calcium carbonate with low (<1 wt.%) Fe and Mg contents, and may be fragments of Muschelkalk (mid-Triassic). Both of the analysed samples plot within the field for limestones and marbles indicating that they are distinct from the magmatic carbonates.

Strontium and neodymium isotopes

Isotopic ratios for Sr and Nd were determined on carbonatitic autoliths, syenites and sanidine megacrysts from the Rockeskyll complex. The data are accompanied by Sr-isotope data for a larger range of syenites and also incorporate existing data from West Eifel volcanic rocks (Kramers *et al.*, 1981, Wörner *et al.*, 1986).

The young age of the West Eifel volcanic rocks (<0.6 Ma; Mertes and Schmincke, 1983) make age corrections to the isotope ratios unnecessary, therefore the measured values (Table 1) can be considered initial. The Sr and Nd isotope chemistry of three carbonatitic autoliths from the Auf Dickel diatreme are plotted in Fig. 5. The East African carbonatite line (EACL) of Bell and Blenkinsop (1989) is also included, and forms a best fit for young African (<40 Ma) carbonatites. The Sr and Nd isotope field for carbonatites from the Kaiserstuhl (southern Germany; Nelson *et al.*, 1988) are also included and along with the Rockeskyll carbonatites define an array, which extends through bulk earth, and is parallel to the EACL. Therefore the carbonatites from Europe do not represent mantle melts from HIMU-EM1 components as suggested by Bell and Blenkinsop (1989) for young carbonatites from Africa, but indicate a source component with a more enriched $^{87}Sr/^{86}Sr$ signature for any given $^{143}Nd/^{144}Nd$ value. The field of Quaternary West Eifel alkali-mafic volcanic rocks is also plotted in Fig. 5 and incorporates unpublished data from leucitite and melilite nephelinite (Rockeskyll Complex), data from Wörner *et al.* (1986) for several centres from the West Eifel and the stippled field is taken from Kramers *et al.* (1981) for alkali-mafic volcanoes at the centre of the West Eifel field and are seen to fall within the same range defined for the carbonatites. The field lies along the average mantle array, an indication that crustal contamination was not important in controlling the present isotopic signatures of the West Eifel eruptives (Kramers *et al.*, 1981) and therefore the values are considered to mirror the true isotopic signature of the sub-Eifel mantle. This is reinforced by Wörner *et al.* (1986) who tested models of contamination between alkali-mafic lavas and the upper and lower crust of the Rhenish Shield, and demonstrated that crustal assimilation has not governed the isotopic composition of the erupted lavas. A common isotopic signature between carbonatites and silicates has also been noted by Bell and Blenkinsop (1989), where nephelinites from Kisingiri volcano also plot on the EACL (Fig. 5). Bell and Peterson (1991) detailed the isotope systematics of nephelinites and carbonatites from Shombole volcano, which also revealed a common signature, and further substantiates a close genetic link.

Feldspathoidal syenites, phonolites and sanidine megacrysts represent the felsic eruptives from the Auf Dickel diatreme and two felsic rocks are plotted in Fig. 5. All the analysed felsic rocks from the Rockeskyll complex have initial $^{87}Sr/^{86}Sr$ ratios that are <0.705 (Table 1), and are consistent with derivation from a low Rb/Sr source, such as the upper mantle or the lower crust (Bell and Powell, 1970). The felsic rocks in Fig. 5 are characterized by the lowest $^{143}Nd/^{144}Nd$ value for a given $^{87}Sr/^{86}Sr$ value, relative to the field of West Eifel nephelinites and carbonatites, suggesting that the felsic rocks cannot be derived by simple fractional crystallization of a nephelinite magma.

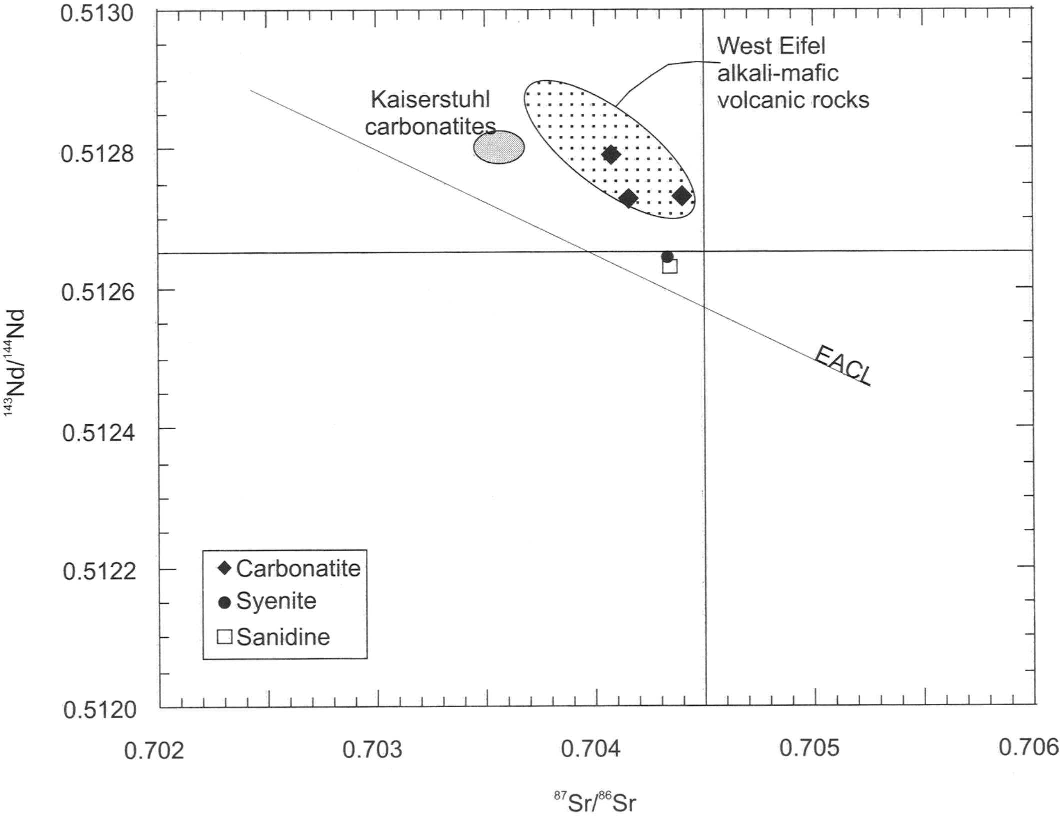


FIG. 5. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ data for West Eifel volcanic rocks.

Petrogenesis

Carbonatite origins

Natural examples and experimental evidence support an origin of carbonate melts in the mantle. Studies by Wallace and Green (1988) demonstrated that dolomitic melts could be produced from mantle peridotite in the presence of CO_2, at pressures >25 kbar, whilst the availability of 'free' CO_2 in the mantle is given credence by Schrauder and Navon (1993) who report solid CO_2 in natural diamonds. Most natural carbonatites are calcic in composition, therefore if they are derived from primary dolomitic melts, a mechanism is required to drive the parent melt toward the more calcic magmas widely reported from the surface. Dalton and Wood (1993) and Sweeney (1994) have both proposed mechanisms that could drive primary carbonate (dolomitic) melts toward more calcic compositions via mantle wallrock reaction or crystallization of Mg-bearing phases during their ascent to the surface. Natural examples supporting a mantle origin of carbonatites include reports of carbonate pockets in mantle xenoliths (e.g. Ionov *et al.*, 1993), interpreted as 'frozen' carbonate melts which are able to move freely in the upper mantle. High-Cr, magnesiochromite in carbonatites from Rufunsa (Bailey, 1989) and Uyannah (Woolley *et al.*, 1991) also confirm an origin of carbonate melts in the mantle.

The autolith mineral assemblage from Auf Dickel represents an erupted melt composition (see also Riley *et al.*, 1996), and is comparable to assemblages from Vúlture, Italy (autoliths of calcite-melilite-haüyne-melanite; A. R. Woolley, pers. comm.) and the bergalite of Kaiserstuhl (calcite-melilite-haüyne nephelinite; Keller, 1984). The Auf Dickel carbonatite has a significant SiO_2 component, a common feature of extrusive calciocarbonatites (Riley *et al.*, 1996), which may be attributed to contamination by silicate xenocryst material, but may indicate that carbonate melts are not restricted to pure carbonate, but that a continuum exists from carbonate to silica undersaturated, alkali-mafic melts (e.g. melilitite). Such rocks are typical associates of carbonatites and are characterized by low silica activity, high activity of CO_2 and the appearance of melilite, leucite, kalsilite and perovskite (Bailey, 1993). The association at Rockeskyll is one of carbonatite and phonolite, coeval with alkali-mafic rocks, characterized by melilite and leucite. The case for a genetic link between melilite and carbonate bearing magmas is strong and has been proposed for the eruptives at Kerimasi, Tanzania (Mariano and Roeder, 1983) and the Kaiserstuhl, Germany (Keller, 1984). The Kaiserstuhl alkaline/carbonatite complex consists of olivine nephelinite, melilitite, tephrite, phonolite and carbonatite, and as such presents parallels to the Quarternary volcanics of Rockeskyll. Keller (1984) proposed a close genetic link between the carbonatite and the calcite-melilite-haüyne nephelinite (bergalite) at Kaiserstuhl. This statement was supported by Schleicher *et al.* (1990) who showed the Sr-isotope systematics of the melilite-bearing lavas and the carbonatite to be consistent with a genetic link, with the bergalite forming the intermediate composition. At Rockeskyll, a close association is also indicated by isotope ranges ($^{87}Sr/^{86}Sr_{carbonatite}$: 0.70408–0.70440; $^{87}Sr/^{86}Sr_{nephelinite}$: 0.7040–0.70494). Such magmas are likely to be derived from a common, enriched source region, although there is no clear evidence that the carbonatite represents an immiscible fraction from a carbonated nephelinite magma.

Syenite-phonolite petrogenesis

The syenite and phonolite xenoliths erupted within the tuffisite ash of the Auf Dickel diatreme are interpreted to represent fragments of a sub-volcanic, carbonatite-syenite complex. Diatreme emplacement may have fragmented a sub-volcanic syenitic body and the erupted xenoliths were rounded during fluidization processes, as the diatreme developed. The variations observed in syenite chemistry (peralkaline-peraluminous) and modal mineralogy (0–20% calcite) indicate that the diatreme has sampled a chemically heterogeneous (possibly zoned) syenite body, which is intimately associated with calciocarbonatite.

Feldspathoidal syenitic plutons are common in alkali-mafic/carbonatite provinces, e.g. Chilwa Island, Malawi (Woolley, 1987; Simonetti and Bell, 1994); Fen, Norway (Andersen, 1988), and petrogenetic models for their origin are varied. Andersen (1988) attributed the association of carbonatite and nepheline syenite of the Fen complex to be the result of shallow level fractional crystallization (clinopyroxene and nepheline) of an ijolite parent, followed by liquid immiscibility to derive the felsic and carbonate rock types. Woolley (1987) envisaged separate magma types to produce the association of carbonatite, nephelinite and phonolite in the Chilwa Island Complex (Malawi), each of the magma types being derived from partial melting at different depths in strongly metasomatized lithosphere. Simonetti and Bell (1994) favoured binary mixing of nephelinite magma and lower crustal granulite to explain the isotope differences between the syenites and alkali mafic rocks in the Chilwa Island complex. The extrusive association of nephelinite-phonolite-carbonatite is also evident at several localities, e.g. Shombole, Kenya (Bell and Peterson, 1991) and Oldoinyo Lengai, Tanzania (Bell and Simonetti, 1996). At both these volcanoes isotope systematics have been used to suggest that the felsic rocks result from interaction between nephelinite and lower crustal granulites.

The isotope evidence from the Rockeskyll Complex does not support a model of simple fractional crystallization of nephelinite magma to derive the Auf Dickel phonolites. For a given $^{87}Sr/^{86}Sr$, the $^{143}Nd/^{144}Nd$ is lower in the felsic rocks (syenite, sanidine) than in the nephelinites and carbonatites (Fig. 5). A similar isotopic pattern is seen in the alkaline rocks of Shombole and Oldoinyo Lengai (see above), where fractional crystallization has also been ruled out and phonolite generation has been attributed to interaction between lower crustal granulites and a nephelinite magma. Testing this model for the Auf Dickel felsic rocks is made difficult by uncertainty surrounding the nature of the lower crust beneath the Eifel (Stosch *et al.*, 1992). Epsilon Nd (present day) values for the Eifel crust (Stosch *et al.*, 1992) vary from *c.* +4 (granulite) to *c.* −7 (metasediment), with the felsic rocks having an εNd value of *c.* 0.

There is increasing evidence supporting the stability of felsic melt in the mantle, which has been confirmed by reports of felsic glasses in peridotite xenoliths (e.g. Edgar *et al.*, 1989; Schiano and Clocchiatti, 1994; O'Connor *et al.*, 1996), with their equilibrium verified by the experimental studies of Draper and Green (1997). Phonolite lava carrying ultramafic xenoliths to the surface (e.g. Wright, 1966) adds support to an origin of felsic melt in the upper mantle. The eruption of large volumes of felsic lava (e.g. Scott, 1980) mean that alternatives to low pressure fractionation need consideration, especially when the mafic parent is not in evidence or is subordinate in volume (e.g. Chilwa Province; Woolley, 1987). Experimental determinations of felsic mineral stabilities in the upper mantle (up to 30 kbar; Ryabchikov *et al.*, 1982) were reviewed by Bailey (1987), who concluded that felsic melt generation in the upper mantle was not only possible, but provided the most plausible explanation of many otherwise puzzling aspects of syenite magmatism. Obviously, felsic melt generation in the upper mantle can only be realised if there is an available source of alkalis and the $a\mathrm{H_2O}$ or halogens is sufficient to stabilize high-$\mathrm{SiO_2}$ melts. Upper (depleted) mantle mineralogies have low or zero abundances of the alkalis, therefore a mechanism is required to enrich mantle domains in those elements incompatible in mantle mineralogies and thus those elements which are mobile in the upper mantle (Bailey, 1987). Such a mechanism may provide a link to the occurrence of sanidine megacrysts, which could represent mantle pegmatites (Aspen *et al.*, 1990), crystallizing from the migration of an aqueous- or halogen-dominated fluid, which are particularly effective at transporting the alkalis and silicon (Ryabchikov *et al.*, 1982).

The phonolite fragments represent the extrusive equivalent of the vishnevite syenites and they may actually preserve phonolitic ejecta, or fragments of dykes emplaced at a higher level to the sub-volcanic syenite body. Their eruption was almost certainly synchronous with the carbonatite activity, invoking parallels to mixed carbonate/felsic volcanism elsewhere (e.g. Mt. Suswa, Kenya; Macdonald *et al.*, 1993).

In summary, two possibilities exist for the origin of the felsic rocks at Auf Dickel: (1) interaction between nephelinite magma and crustal rocks; or (2) a direct origin from the upper mantle. Uncertainty surrounding the crustal component of the Eifel (Stosch *et al.*, 1992) make interpretations considering interaction with a nephelinite magma difficult, although it cannot be ruled out. An origin of felsic melts from a strongly metasomatized upper mantle is given support by evidence of silicic melts trapped in mantle xenoliths from the West Eifel (e.g. Edgar *et al.*, 1989). Also, the small volume of phonolitic (and carbonatitic) rocks present in the West Eifel suggest a more exotic origin than interaction between nephelinite and sub-Eifel crust, considering the widespread occurrence of alkali-mafic lavas throughout the West Eifel.

Discussion

The association of carbonate, felsic and alkali-mafic magma types at Rockeskyll is unique in the West Eifel, and coupled with the presence of mantle-derived material, a full evaluation of processes in the sub-continental mantle can be made.

There is now little dispute over a close link between the derivation of carbonate magmas within the lithospheric mantle; with evidence, not only from magmatic associations, but direct evidence from carbonatite erupting mantle material (Bailey, 1993). However, a direct association between felsic melts and the upper mantle has received less support, as they are widely considered to be products of simple fractional crystallization of a mafic parent, or involve some process of crustal interaction. The evidence summarized in the section on syenite petrogenesis provides evidence for felsic melt generation (and stability) in the upper parts of the lithospheric mantle, which may provide the most plausible explanation for the Rockeskyll eruptives. The recognition of carbonate and felsic melts in the upper mantle (Schiano *et al.*, 1994), and their known ability to concentrate the incompatible elements led to the corollary that they could be responsible for the enrichment of the lithospheric mantle, necessary for the production of alkali-mafic magmas by small degrees of mantle melting. The West Eifel alkaline field mirrors the above association, with the predominance of alkali-mafic lavas and the subordinance of carbonatite and phonolite. The erupted mantle xenoliths from throughout the field show evidence of enrichment (e.g. Lloyd and Bailey, 1975) and preserve pockets of carbonate minerals (O'Connor *et al.*, 1996) and felsic glass (Edgar *et al.*, 1989), interpreted as trapped mantle melts that were responsible for the enrichment events (metasomatism).

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