American Mineralogist, Volume 60, pages 722–725, 1975

Occurrences of Rhönite in Alkalic Lavas of the McMurdo Volcanic Group, Antarctica, and Dunedin Volcano, New Zealand

PHILIP R. KYLE,

Department of Geology, Victoria University,
Wellington, New Zealand

AND RICHARD C. PRICE[1]

Department of Geology, University of Otago,
Dunedin, New Zealand

Abstract

Occurrences of rhönite are reported in alkalic lavas of the McMurdo Volcanic Group (Hut Point Peninsula, Antarctica) and Dunedin Volcano (New Zealand). Electron microprobe analyses increase the range of composition reported for rhönite, with the Antarctic examples having higher TiO_2, and the Dunedin example higher Na_2O than other terrestrial rhönites. Detectable quantities of Cr_2O_3 (average 0.11 percent) and NiO (0.06 percent) are recorded for the first time. The rhönite shows no compositional variation toward aenigmatite.

Introduction

Rhönite is a groundmass constituent of lavas at Hut Point Peninsula, Ross Island, Antarctica. The mineral was discovered during an electron microprobe investigation of core samples from two holes drilled by the Dry Valley Drilling Project (DVDP) at Hut Point Peninsula (Mudrey *et al*, 1973; Treves and Kyle, 1973; Kyle and Treves, 1974a). This is the first reported occurrence in the McMurdo Volcanic Group and also in Antarctica. In the southern hemisphere the only other previously reported occurrence of rhönite has been in the Otago volcanics, New Zealand, where Benson (1939) reported it as an alteration product after kaersutite. The literature on rhönite has been reviewed by Cameron, Carman, and Butler (1970). Other reported occurrences are in the *Allende* meteorite (Fuchs, 1971) and metaphonolite from Puy de Saint-Sandoux (Grünhagen and Seck, 1972). The crystallography has been discussed by Walenta (1969). As very few analyses of rhönite have been published, the electron microprobe analyses reported here give a further indication of the range in composition.

Occurrence

The Late Cenozoic McMurdo Volcanic Group (Harrington, 1958; Nathan and Schulte, 1968) consists of undersaturated alkaline volcanics which range in composition from alkali olivine basalt and basanite (basanitoid) to trachyte and phonolite. At Hut Point Peninsula the lavas are basanites (basanitoids), nepheline hawaiite, nepheline mugearite, nepheline benmoreite, and phonolite which range in age from 0.4 to greater than 1.2 m.y. (Forbes, Turner, and Carden, 1974; Kyle and Treves, 1974b). Rhönite occurs in unit 37 of DVDP 1, units 12 and 13 of DVDP 2 (Treves and Kyle, 1973), and units 10–15 of DVDP 3 (Kyle and Treves, 1974b). A detailed petrographic examination of surface flows revealed no primary rhönite; however, a fine grained mineral occurring as an alteration product of kaersutite in some of the lavas intermediate in composition between the basanite and phonolite may be rhönite.

Rhönite grains in three samples (DVDP 1–121.88 m; DVDP 2–99.34 m and 103.15 m) of porphyritic olivine (Fo_{77-87})-titan-salite (Wo_{48-53}; Fs_{10-16}, En_{34-40}) basanite (Table 1) were examined by electron microprobe (Kyle, 1974). In DVDP 1–121.88 m rhönite is abundant as euhedral prismatic microphenocrysts which rarely reach 0.2 mm and average 0.1 to 0.05 mm in length. Abundance decreases in DVDP 2 samples where the microphenocrysts are much finer grained (0.01 mm), are irregular and ragged in form, and occur in a subophitic groundmass of plagioclase, pyroxene, and

---

[1] Present address: Department of Geology, School of Physical Sciences, La Trobe University, Bundora, Victoria 3083, Australia.

Table 1. Analyses and CIPW Norms for Dunedin and DVDP Host Rocks in Which Rhönite Occurs

	Wt Percent			CIPW Norms	
	1	2		1	2
SiO_2	47.57	41.72	Or	12.76	8.80
TiO_2	2.21	4.18	Ab	30.57	3.79
Al_2O_3	16.47	13.03	An	13.78	17.55
Fe_2O_3	4.27	4.25	Ne	8.74	11.84
FeO	7.32	7.66	Di	11.48	26.66
MnO	0.21	0.18			
MgO	3.47	12.03	Ol	7.07	15.18
CaO	6.68	11.47	Il	4.20	7.94
Na_2O	5.52	3.03	Mt	6.19	6.16
K_2O	2.16	1.49	Ap	1.90	1.97
P_2O_5	0.82	0.85	Other	3.40	0.08
H_2O+	2.83	0.08*			
H_2O-	0.42	-	Total	100.09	99.97
S	0.15	-			
Total	100.10	99.97			

1. Nepheline hawaiite; Pulling Point, Otago Harbour, New Zealand.
2. Basanite (mean of 3 analyses); DVDP 1 and 2, Hut Point Peninsula, Antarctica.

* Loss on ignition 1000°C.

opaques. In DVDP 2–99.34 m the rhönite is usually intergrown with or surrounded by groundmass pyroxene. In the Dunedin District, South Island, New Zealand, rhönite occurs within alteration rims on kaersutite crystals which, together with titaniferous augite, olivine, minor intermediate plagioclase, apatite, and titanomagnetite, makes up small (1 cm) coarse-grained xenoliths in a nepheline hawaiite flow at Pulling Point in Otago Harbour. The host rock (Table 1) is composed of a groundmass of plagioclase (An_{40-50}), pale green clinopyroxene, interstitial nepheline, and homogeneous titanomagnetite in which are set phenocrysts of oscillatory and sector-zoned titan-augite, olivine (Fo_{50}), and kaersutite (α = pale yellow, β = pale reddish brown, γ = pale reddish brown).

Grains of rhönite are too small to allow determination of precise optical properties. In standard thin sections it is opaque but in thin sections less than 20 μm thick it shows strong pleochroism from deep greenish brown to opaque, similar to that reported by Cameron *et al* (1970) and Walenta (1969).

Composition

Analyses were made using a JEOL JXA-5A electron microprobe with 15 kV accelerating potential, 2–3 × 10^{-8} amp specimen current (on periclase) and a beam diameter of 1–2 μm. The empirical correction procedure of Bence and Albee (1968) was used. Standards, alpha correction factors, and analytical techniques are given by Kushiro and Nakamura (1970).

Typical analyses of three DVDP samples and one Dunedin sample, and five previously published analyses of rhönite, are presented in Table 2. With the exception of MgO and Cr_2O_3, electron microprobe scans across grains indicated a uniform composition. Almost all the grains examined contained detectable (detection limit was 0.03 percent) Cr_2O_3 and NiO, which is the first time they have been analyzed in rhönite.

Compared to other terrestrial rhönite the Antarctic samples show higher TiO_2, Na_2O, and lower SiO_2

Table 2. Analyses of Rhönite

	1	2	3	4	5	6	7	8	9
SiO_2	23.8	23.7	23.2	28.58	24.82	24.42	30.90	29.8	19.1
Al_2O_3	17.0	16.8	17.4	13.35	17.24	17.25	17.65	13.6	28.9
TiO_2	11.6	11.9	12.0	10.70	9.09	9.46	8.04	10.2	16.8
Fe_2O_3	-	-	-	-	9.48	11.69	6.80	21.2_T	-
FeO	21.3_T	21.0_T	20.9_T	22.49_T	15.98	11.39	15.20	-	1.9_T
MnO	0.19	0.16	0.18	0.17	0.26	tr	-	0.1	-
MgO	12.7	13.05	12.6	12.09	10.67	12.62	9.08	14.4	15.7
CaO	11.8	12.15	12.2	10.23	11.97	12.43	12.20	11.4	17.9
Na_2O	0.96	0.97	0.89	2.11	0.72	0.67	0.76	-	-
K_2O	-	-	-	0.02	0.02	0.63	0.61	-	-
Cr_2O_3	n.d.	0.06	0.15	-	-	-	-	-	-
NiO	0.10	0.04	0.03	-	-	-	-	-	-
V_2O_3	-	-	-	-	-	-	-	-	0.7
P_2O_5	-	-	-	-	0.03	-	-	-	-
H_2O+	-	-	-	-	0.35	-	0.20	-	-
H_2O-	-	-	-	-	0.06	-	-	-	-
Total	99.45	99.83	99.55	99.74	100.69	100.56	101.44	100.7	101.0
Number of Cations on the Basis of 40(0)									
Si	6.536	6.484	6.367	7.785	6.674	6.535	8.032	7.608	4.788
Al	5.502	5.417	5.628	4.285	5.464	5.441	5.408	4.092	8.538
Ti	2.396	2.448	2.476	2.191	1.839	1.904	1.572	1.958	3.167
Fe^{3+}	-	-	-	-	1.919	2.354	1.330	4.073	-
Fe^{2+}	4.892	4.805	4.797	5.123	3.593	2.549	3.304	-	0.398
Mn	0.044	0.037	0.042	0.039	0.060	-	-	0.022	-
Mg	5.199	5.322	5.155	4.909	4.277	5.035	3.517	5.481	5.867
Ca	3.472	3.561	3.587	2.986	3.448	3.564	3.398	3.118	4.808
Na	0.511	0.514	0.474	1.116	0.375	0.348	0.383	-	-
K	-	-	-	0.005	0.006	0.215	0.202	-	-
Cr	-	0.013	0.032	-	-	-	-	-	-
Ni	0.022	0.009	0.007	-	-	-	-	-	-
V	-	-	-	-	-	-	-	-	0.141
P	-	-	-	-	0.006	-	-	-	-
OH	-	-	-	-	0.628	-	0.347	-	-
Z	12.000	11.901	11.995	12.000	12.000	11.976	12.000	11.700	12.000
Y	12.591	12.634	12.509	12.332	11.832	11.842	11.163	11.534	10.899
X	3.983	4.075	4.061	4.107	3.829	4.127	3.983	3.118	4.808
Sum	28.574	28.610	28.565	28.439	27.661	27.945	27.146	26.352	27.707

(1) DVDP 1 - 121.88 m; representative analysis.
(2) DVDP 2 - 99.34 m; representative analysis.
(3) DVDP 2 - 103.15 m; representative analysis.
(4) Pulling Point, Otago Harbour, Dunedin, New Zealand; representative analysis.
(5) Big Bend, Texas (Cameron, Carman and Butler, 1970).
(6) Rhön, Germany (Soellner, 1907).
(7) Saint Sandoux, France (Lacroix, 1909).
(8) Haute-Loire, France, electron microprobe analysis (Babkine, et al. 1967).
(9) Allende meteorite, electron microprobe analysis (Fuchs, 1971).

T = total iron expressed as FeO or Fe_2O_3; n.d. = not detected (<0.03%).
\- = not determined.

contents. The Dunedin rhönite is noticeably enriched in Na_2O with a related deficiency in CaO, compared with the other analyses. Total iron is slightly higher than previously reported in other rhönites, and the other elements fall within the established limits. Rhönite in the *Allende* meteorite (9, Table 2) differs markedly from the Antarctic and Dunedin samples and from all terrestrial samples, particularly with regard to total Fe.

Structural formulae were calculated on the basis of 40(O) as recommended by Kelsey and McKie (1963) and Cameron *et al* (1970). The ideal formula of $X_4Y_{12}Z_{12}O_{40}$ requires a total of 28 cations; however, rhönites 1, 2, 3, and 4 (Table 1) all have cation totals exceeding 28 with an excess of *Y* cations, thus indicating that the Antarctic and Dunedin rhönites probably contain Fe^{3+} in the formula. The amount of Fe_2O_3 necessary for the DVDP samples and the Dunedin sample to achieve stoichiometry (*i.e.*, a cation sum of 28) was calculated (Table 3); an average of about 8 percent Fe_2O_3 is indicated for the DVDP samples and about 6 percent for the Dunedin sample. Noticeable, however, is the decrease in the *Z* cations (Si+Al) while *Y* still exceeds 12. This implies that there may be a significant amount of Fe^{3+}, as suggested by Cannillo *et al* (1971) for aenigmatite, or Ti in the tetrahedral *Z* site.

Cameron *et al* (1970) discussed the suggestion of Fleischer (1936) that rhönite and aenigmatite form a substitution series. The rhönite examined in this study shows no evidence of compositional variation towards aenigmatite and thus strengthens the suggestion of Cameron *et al* (1970) that there is only limited solid solution at magmatic temperatures.

Discussion

The crystallization of primary rhönite like the isomorphic aenigmatite (Lindsley, 1970; Hodges and Barker, 1973) is probably controlled by such factors as oxygen fugacity, temperature, and the activity of silica and titanium. In the Antarctic samples, estimates have been made of oxygen fugacity and temperature (Table 4) using co-existing groundmass magnetite–ilmenite pairs (Buddington and Lindsley, 1964) that probably crystallized at the same time or later than the rhönite. Silica activity (Table 4) was calculated using the above data and the composition of olivine in the groundmass or at the rim of phenocrysts (Table 4). Both oxygen fugacity and silica activity are typical of basanites and nepheline-rich basaltic lavas (Anderson, 1968; Carmichael and Nicholls, 1967; Carmichael, Nicholls, and Smith, 1970). Crystallization of primary rhönite cannot therefore be explained in terms of unusual temperature, oxygen fugacity, or silica activity.

TABLE 3. Recalculated Fe_2O_3 and FeO assuming Stoichiometry of Rhönite in DVDP and Dunedin Samples

Sample number*	1	2	3	4
Fe_2O_3	7.89	8.45	7.78	6.10
FeO	14.2	13.4	13.9	17.0
Analysis total	100.24	100.68	100.33	100.36
Cation totals				
Z	11.797	11.647	11.758	11.912
Y	12.302	12.366	12.262	12.052
X	3.903	3.989	3.981	4.037

* Same as Table 2.

TABLE 4. Oxygen Fugacity, Temperature, and Silica Activity Calculated for the Groundmass of DVDP Basanites

Sample Number	Magnetite Usp %*	Ilmenite Hm %*	Olivine Fa %	T°C	log fo_2	log a_{SiO_2}**
1 - 121.88	68.7	6.2	22	985	- 11.5	- 1.05
2 - 99.34	69.1	6.1	-	970	- 11.8	-
2 - 103.15	61.3	6.7	22	955	- 12.0	- 1.12

* Magnetite and ilmenite electron microprobe analyses recalculated to end members using method of Carmichael (1967).

** Calculated using the reaction
$2/3\ Fe_3O_4 + SiO_2 = Fe_2SiO_4 + 1/3\ O_2$ (Nicholls et al, 1971).

In the Dunedin nepheline hawaiite, rhönite has obviously formed as a result of reaction between earlier formed kaersutite and the undersaturated host liquid. Groundmass oxides are homogeneous titanomagnetites, indicating generally low fO_2 conditions (Watkins and Haggerty, 1967).

Acknowledgments

The authors are indebted to Dr. Yasuo Nakamura for instruction on the use of the electron microprobe and to Professor D.S. Coombs for allowing the use of the instruments at Otago University. They extend thanks to Professor Coombs and to Dr. T. Seward for critically reading the manuscript. Core samples were obtained through the assistance of NSF (U.S.A.), D.S.I.R. (N.Z.), and the Japan Polar Research Centre. Financial support was provided by a Victoria University Internal Research Grant.

References

ANDERSON, A. T. (1968) The oxygen fugacity of alkaline basalt and related magmas, Tristan da Cunha. *Am. J. Sci.* **266,** 704–727.

BABKINE, J., F. CONQUERE, J. C. VILMINOT, AND P. K. DUONG (1964) Sur un nouveau gaisement de rhönite (*Monistrd-d'Allier,* Haute Loire). *C. R. Acad. Sci., Paris, Ser D.* **258,** 5479–5481.

BENCE, A. E., AND A. L. ALBEE (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76,** 382–403.

Benson, W. N. (1939) Mineralogical notes from the University of Otago, N. Z. No. 3: Kaersutite and other brown amphiboles in the Cainozoic igneous rocks of the Dunedin District. *Trans. R. Soc. N.Z. (Geol.)* **69**, 283–308.

Buddington, A. F., and D. H. Lindsley (1964) Iron-titanium oxide minerals and synthetic equivalents. *J. Petrol.* **5**, 310–357.

Cameron, K. L., M. F. Carman, and J. C. Butler (1970) Rhönite from Big Bend National Park, Texas. *Am. Mineral.* **55**, 864–874.

Cannillo, E., F. Mazzi, J. H. Fang, P. D. Robinson, and Y. Ohya (1971) The crystal structure of aenigmatite. *Am. Mineral.* **56**, 427–446.

Carmichael, I. S. E. (1967) The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesium silicates. *Contrib. Mineral. Petrol.* **14**, 36–64.

———, and J. Nicholls (1967) Iron titanium oxides and oxygen fugacities in volcanic rocks. *J. Geophys. Res.* **72**, 4665–4687.

———, ———, and A. L. Smith (1970) Silica activity in igneous rocks. *Am. Mineral.* **55**, 246–263.

Fleischer, Michael (1936) The formula of aenigmatite. *Am. J. Sci.* **32**, 323–348.

Forbes, R. B., D. L. Turner, and J. R. Carden (1974) Age of trachyte from Ross Island, Antarctica. *Geology,* **2**, 297–298.

Fuchs, L. H. (1971) Occurrence of wollastonite, rhönite, and andradite in the *Allende* meteorite. *Am. Mineral.* **56**, 2053–2068.

Grünhagen, H., and H. A. Seck (1972) Rhönit aus einem Melaphonolith vom Puy de Saint-Sandoux (Auvergne). *Tschermaks Mineral. Petrogr. Mitt.* **18**, 17–38.

Harrington, H. J. (1958) Nomenclature of rock units in the Ross Sea region, Antarctica. *Nature (London),* **182**, 290.

Hodges, F. N., and D. S. Barker (1973) Solid solution in aenigmatite. *Carnegie Inst. Wash. Year Book,* **72**, 578–581.

Kelsey, C. H., and D. McKie (1963) The unit cell of aenigmatite. *Mineral. Mag.* **33**, 986–1001.

Kushiro, I., and Y. Nakamura (1970) Petrology of some lunar crystalline rocks. *Proc. Apollo 11 Lunar Sci. Conf.* **1**, 607–626.

Kyle, P. R. (1974) Electron microprobe analyses of minerals in core samples from Dry Valley Drilling Project (DVDP) Holes 1 and 2, Ross Island, Antarctica. *Dep. Geol. Victoria Univ. of Wellington Publ.* **4**, 27 p.

———, and S. B. Treves (1974a) Geology of DVDP 3, Hut Point Peninsula, Ross Island, Antarctica. *Dry Valley Drilling Project Bulletin No.* **3** (Northern Illinois University), 13–48.

———, and ———(1974b) Geology of Hut Point Peninsula. *Antarctic J. U.S.* **9**, 232–234.

Lacroix, M. A. (1909) Note sur la rhönite du Puy de Barneire a Saint-Sandoux. *Bull. Soc. Fr. Mineral. Cristallogr.* **32**, 325–331.

Lindsley, D. H. (1970) Synthesis and preliminary results on the stability of aenigmatite ($Na_2Fe_2TiSi_6O_{20}$). *Carnegie Inst. Wash. Year Book,* **69**, 188–190.

Mudrey, M. J., Jr., S. B. Treves, P. R. Kyle, and L. McGinnis (1973) A frozen jig-saw puzzle—first bedrock coring in Antarctica. *Geotimes,* **18**, 14–17.

Nathan, S., and F. J. Schulte (1968) Geology and petrology of the Campbell-Aviator divide, Northern Victoria Land, Antarctica. Part 1. Post paleozoic rocks. *New Zealand J. Geol. Geophys.* **11**, 940–975.

Nicholls, J., I. S. E. Carmichael, and J. C. Stormer, Jr. (1971) Silica activity and P_{total} in igneous rocks. *Contrib. Mineral. Petrol.* **33**, 1–20.

Soellner, J. (1907) Üeber Rhönit, ein neues änigmatitähnliches Mineral und über das Vorkommen und über die Verbreitung desselben in basaltischen Gesteinen. *Neues Jahrb. Mineral. Beil-Bd.* **24**, 475–547.

Treves, S. B., and P. R. Kyle (1973) Geology of DVDP 1 and 2, Hut Point Peninsula, Ross Island, Antarctica. *Dry Valley Drilling Project Bulletin No.* **2** (Northern Illinois University), 11–82.

Walenta, Von Kurt (1969) Zur kristallographie des Rhönits. *Z. Kristallogr.* **130**, 214–230.

Watkins, N. D., and S. E. Haggerty (1967) Primary oxidation variation and petrogenesis in a single lava. *Contrib. Mineral. Petrol.* **15**, 251–271.

Manuscript received, October 28, 1974; accepted for publication, December 17, 1974.