# Journal of the Iowa Academy of Science: JIAS

Volume 98 | Number

Article 8

1991

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## **Recommended Citation**

Windom, Kenneth E.; Seifert, Karl E.; and Anderson, Raymond R. (1991) "Studies of the Precambrian Geology of Iowa: Part 2. The Matlock Keratophyre," *Journal of the Iowa Academy of Science: JIAS, 98(4),* 178-181.

Available at: https://scholarworks.uni.edu/jias/vol98/iss4/8

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# Studies of the Precambrian Geology of Iowa: Part 2. The Matlock Keratophyre

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Felsic pyroclastic rock occurs in the Precambrian basement in northwestern Iowa. This rock was recovered by drilling and originally logged as rhyolite; however it is severely depleted in  $K_2O$ , Rb, Ba, Cs, and other mobile elements and is more properly called keratophyre. The volcanic unit lies atop a layered mafic/ultramafic complex and contains xenoliths of gabbro apparently derived from the layered body. These xenoliths are severely altered and are composed of secondary hydrated and carbonated minerals. The gabbros are enriched in incompatible trace elements, whose abundance patterns complement those of the keratophyre. Trace element abundance patterns for the keratophyre suggest it was derived by partial melting in a subduction zone. The keratophyre is comparable to rhyolite exposed in Wisconsin in terms of age, stratigraphic position, and low-grade metamorphism, although it cannot be established whether or not they are related in any way. INDEX DESCRIPTORS: Precambrian, keratophyre, volcanic rocks.

Felsic pyroclastic rock was recovered by drilling near the town of Matlock, IA in 1963 as part of a mineral exploration project of New Jersey Zinc Company (Fig. 1). The pyroclastics were originally logged as rhyolite. They comprise flow breccia at the base that grades upward into devitrified tuff. The volcanic rock unconformably overlies an older layered mafic-ultramafic complex (Tvrdik, 1983; Windom et al., 1991) (Fig. 2); gabbroic xenoliths from the layered complex are contained within the volcanic rocks.

Tvrdik (1983) gave macroscopic and microscopic descriptions of the volcanics. We have re-examined them microscopically and have also obtained whole-rock major and trace element analyses of the pyroclastics and gabbroic xenoliths contained within them.

#### PETROLOGY AND GEOCHEMISTRY

The pyroclastics consist of rounded albite phenocrysts  $(An_{0-7})$  up to 15 mm in length, commonly twinned and zoned, surrounded by finegrained quartz, sericite, plagioclase, and hematite; Tvrdik (1983) reported the presence of minor K-feldspar in the groundmass. The albite phenocrysts are commonly altered to sericite or replaced by calcite.

Whole-rock chemical analyses are given in Tables 1 and 2. Analytical procedures are the same as described in Windom et al. (1991). The volcanic rocks are high in felsic components except for extreme depletion in  $K_2O$ , Rb, Ba, and Cs. These compositions are thus representative of keratophyre instead of rhyolite and this volcanic unit is herein named the Matlock keratophyre.



Fig. 1. Location of core holes, drilled by New Jersey Zinc Company in 1963 for iron-ore exploration, relative to the Matlock magnetic anomaly. Magnetic contours (dashed lines) in gammas.

The two analyzed samples are very consistent in concentrations of major elements  $SiO_2$ ,  $TiO_2$ ,  $Al_2O_3$ , FeOt, and  $K_2O$  but show considerable differences in CaO and Na<sub>2</sub>O, and, to a lesser extent, MgO. Significant differences in trace element concentrations also exist for Ba,





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Fig. 2. Cross section of basement geology in northwestern Iowa reconstructed from drill core recovered by New Jersey Zinc Company in 1963.

	Keratophyre		Gabbro Xenoliths					
	С5-659ь	C5-848	C5-855	<b>C5-</b> 971	C5-1015			
SiO <sub>2</sub>	70.0	70.0	42.7	51.2	48.2			
TiO <sub>2</sub>	0.31	0.29	0.30	0.20	1.24			
$Al_2\bar{O}_3$	12.2	12.2	20.4	24.2	24.5			
$Cr_2O_3$	< 0.01	<0.01	< 0.01	< 0.01	< 0.01			
FeŌt	3.16	3.32	4.11	3.40	4.82			
MnO	0.08	0.06	0.09	0.05	0.06			
MgO	1.99	2.29	3.65	1.96	1.89			
CaO	5.07	2.31	12.2	8.54	8.33			
Na <sub>2</sub> O	3.97	5.67	1.82	3.94	2.63			
K <sub>2</sub> O	0.18	0.20	4.22	2.85	3.73			
$P_2O_5$	0.07	0.06	0.03	0.07	0.02			
LOI	2.62	2.70	10.1	3.31	3.77			
Sum	99.7	99.1	99.6	99.7	99.2			
H <sub>2</sub> O+	1.7	1.4	2.8	1.5	1.5			
CÕ <sub>2</sub>	1.11	1.40	6.92	0.86	0.86			
- Normative Mineralogy								
QZ	33.74	27.84	_					
OR	1.10	1.23	5.51	17.46	23.09			
AB	34.60	49.75	_	27.65	19.34			
AN	15.39	7.51	39.10	41.39	43.14			
CO			—		1.09			
LC			17.51	—	—			
DI	8.27	3.25	23.01	1.70				
ΗY	5.40	8.95	_		_			
OL	_		3.82	6.71	7.57			
NE			9.31	3.74	2.15			
MT	0.72	0.76	1.01	0.78	1.11			
IL	0.61	0.57	0.64	0.39	2.47			
AP	0.17	0.15	0.08	0.17	0.05			

Table 1. Major Element Compositions and Normative Mineralogies<sup>a</sup> of the Matlock Keratophyre and Gabbro Xenoliths (in weight percent).

<sup>a</sup>Normative mineralogies calculated assuming  $Fe_2O_3/FeO = 0.15$ . <sup>b</sup>Sample numbers refer to core hole and depth below the surface (in feet), i.e., sample C5-659 was taken 659 feet from the top of core C-5.

Sr, Eu, Lu, Co, and Cr, and less so for Th, Ta, La, Ce, Sm, Tb, Yb, Sc, and Ni.

Low abundances of large ion lithophile elements (LILE) are characteristic of keratophyre and several explanations for this phenomenon have been postulated. Experimental studies (Dixon and Rutherford, 1979; Spulber and Rutherford, 1983) have shown that K2O-poor SiO2-rich rocks can be produced by 1) fractional crystallization of tholeiitic basalt at shallow depths in the earth's crust or 2) by liquid immiscibility at fluid pressures greater than 2 kbar. Another explanation for the generation of keratophyre involves alteration of rhyolites by reaction with seawater to remove K2O, Rb, and presumably Ba and Cs (Coleman and Donato, 1979) or by a low-temperature metamorphic/ metasomatic event (Hughes, 1973). Hughes (1973) argued that such low-temperature metamorphism commonly leaves the original rock texture intact, as is seen in thin sections of the Matlock keratophyre. The compositions of the Matlock keratophyre fall outside the spectrum of normal igneous rocks (Hughes, 1973), plotting instead in the field representative of metamorphosed/metasomatized rocks (Fig. 3).

A plot of selected normalized trace element concentrations of the keratophyre (Fig. 4) yields a pattern very similar to S-type felsic rocks related to subduction (Thompson et al., 1984), except for the extreme depletion of K and Rb and the lesser depletion of Ba. Especially

	Keratophyre		Gabbro Xenoliths		
	C5-659	C5-848	C5-855	<b>C5-</b> 971	C5-1015
Ba	91	55	668	322	467
Rb	2	4	140	85	119
Th	9.01	7.25	0.44	1.11	0.40
Nb	14	13	3	2	4
Ta	0.92	0.76	0.10	0.13	0.28
La	46.3	32.0	27.8	15.6	10.6
Ce	96.5	73.2	39.0	27.7	17.0
Sr	167	95	147	326	356
Sm	8.85	6.79	4.45	3.77	2.15
Eu	1.67	0.99	2.97	2.83	5.72
Zr	254	221	22	27	31
Hf	7.07	6.05	0.53	0.82	0.73
Tb	1.04	0.80			
Y	44	34	25	12	11
Yb	3.77	2.88	0.92	1.11	0.78
Lu	0.70	0.42	0.18	0.17	0.15
Sc	7.3	5.3	27.9	8.09	13.3
Co	7.0	3.9	16.6	7.3	20.1
Cr	5.9	18.5	17.4	1.5	1.5
Ni	0.92	0.76			
Cs	0.13	0.16	4.57	1.94	3.02

 Table 2. Trace Element Concentrations of the Matlock

 Keratophyre and Gabbro Xenoliths (in parts per million)

diagnostic of a subduction-related environment is the depletion of Nb and Ta. Rare earth element (REE) abundances in the keratophyre compare well to the other S-type rocks shown in Figure 4. Normalized concentrations of REE follow a nearly linear pattern when plotted versus field strength of the element, suggesting that these elements have been relatively immobile during alteration, an observation in agreement with the findings of REE mobility of Barovitch and Patchett (1990).

Three gabbro clasts contained within the keratophyre were also analyzed. These xenoliths are interpreted to have come from the mafic portion of the underlying Otter Creek layered igneous complex. However, significant compositional differences occur between the clasts and the *in situ* samples reported by Windom et al. (1991). In

14 NEPHELINE IONOLITE 12 TRACTUTE Na 2<sup>0</sup> 10 RHOLTE + 8 LATTE к,0 RHYODACITE 6 ANDESITE 3 4 ALKALI BASAL ٧t. HIGH RASAL THOLEITE 2 0 30 40 50 60 70 80 90 100 20 10 0  $100 \times K_2O/(K_2O + Na_2O)$ 

Fig. 3. Diagram of total alkalis vs. proportion of  $K_2O$  to total alkalis showing Matlock keratophyre (pluses) relative to the spectrum of normal igneous rocks (from Hughes, 1973).

Fig. 4. "Spidergram" of normalized values of selected trace element abundances in Matlock keratophyre (pluses) relative to S-type felsic rocks reported by Thompson et al., 1984 (stippled area). Note severe

depletion of Ba, Rb, and K. Normalization factors taken from

Thompson et al. (1984).

particular, incompatible elements such as K, Ba, Rb, Th, La, Ce, Sr, Sm, Eu, Zr, Hf, Y, Yb, Lu, and Cs are enriched in the xenoliths whereas elements such as Mg, Ca, Co, and Cr, which are more compatible, are depleted. The clasts contain abundant modal carbonate (calcite and dolomite); carbonate veins were avoided to the extent possible when preparing these samples for analysis, but one clast yielded a high  $CO_2$  content despite these efforts. This sample also contains the highest concentration of MgO, CaO, Ba, Rb, La, Ce, Sm, and Cs of any rock analyzed (clast or *in situ* gabbro).

Normalized values of selected trace element abundances in the clasts are plotted in Figure 5 and compared to the range of values for the layered gabbros (Windom et al., 1991). This figure illustrates the considerable enrichment, up to two orders of magnitude, in the xenoliths. The enrichment is especially pronounced for the large ion lithophile elements (LILE) and the light rare earth elements (LREE).

Comparison of Figures 4 and 5 reveals a complementary nature to the patterns of the keratophyre and altered gabbro clasts, especially for the LILE. Combining this observation with the previous discussion concerning depletion of LILE in the keratophyre and the enrichment in the gabbro clasts suggests that the volcanic rock and enclosed gabbro xenoliths acted as a source and reservoir, respectively, for the highly mobile elements, especially the LILE, i.e., depletion of highly mobile elements in the felsic rocks was accompanied by a concomitant increase in the gabbro clasts. The volcanic pile/enclosed gabbro xenoliths thus acted as at least a partially closed system during alteration. The observation of limited depletion of LREE in the keratophyre versus significant enrichment in the gabbro clasts can be explained by noting that the volume of the keratophyre greatly exceeds that of the xenoliths so that, although the clasts have been enriched relative to the in situ gabbro, the absolute abundance of LREE in the altered gabbro is less than that in the keratophyre.

It appears the mobile elements were dissolved in a fluid phase and transported to the clasts where they were incorporated in secondary minerals. The abundant carbonate veins in the gabbro clasts, along with hydrous secondary minerals such as epidote, chlorite, and uralitic amphiboles indicate that the alteration fluid contained substantial CO<sub>2</sub>

Fig. 5. "Spidergram" of normalized values of selected trace element abundances of gabbro xenoliths (asterisks) relative to unaltered gabbro from the underlying Otter Creek layered igneous complex reported by Windom et al., 1991 (stippled area). Normalization factors same as in Fig. 4; note different scale on ordinate compared to Fig. 4.

along with  $H_2O$ . The factors controlling the precipitation of phases containing the mobilized LILE may have been the abundance of Ca, Fe, and Mg in the gabbro relative to the felsic rocks. These elements are necessary for the secondary minerals found in the gabbro clasts and formation of these minerals would fix the  $H_2O$  and  $CO_2$  components of the volatile phase and the dissolved LILE in crystalline lattices.

Geochronological data for the Matlock keratophyre, based on U-Pb ages obtained from zircons, have been reported by Van Schmus and Wallin (1991). They determined a crystallization age of  $1782 \pm 10$  Ma for these volcanics. Earlier determinations (Van Schmus et al., 1987) yielded ages of approximately 2.3 Ga, but it was later established that this age was spurious and caused by contamination from xenocrystic cores in many of the younger zircons. (A second population of brownish zircon, which yielded an Archean age, was also found in the keratophyre, but this has been interpreted as having been incorporated in the magma during eruption, coming either from the walls of the conduit through the Archean country rock or from detrital grains on the ground surface that were picked up by the pyroclastic flows). The cores imply the presence of pre-exisitng chemically evolved material in the source region of the keratophyre, although the exact nature of the parental material is uncertain (see Van Schmus and Wallin, 1991, for a more detailed discussion). These observations are consistent with the geochemical evidence suggesting the keratophyre is related to S-type granites derived by partial melting in a subduction-type environment.

#### COMPARISON WITH OTHER FELSIC VOLCANICS

Other felsic rocks similar to the Matlock keratophyre in age and inferred stratigraphic position occur near Marquette, Wisconsin (Smith, 1978a, b; Van Schmus, 1978). Van Schmus (1978) determined a crystallization age of  $1760 \pm 10$  Ma for a series of granites and rhyolites in the Fox River Valley of Wisconsin using U-Pb isotopes in zircons. He interpreted a date of 1630 Ma, determined earlier using Rb-Sr isotopes (Van Schmus et al., 1975), as representing a later metamorphic event. Thus, in addition to having comparable crystallization ages, both the Matlock keratophyre and the Wisconsin





rhyolites show evidence of later low-grade metamorphism, although the Matlock keratophyre was more severely altered during its metamorphism than were the Wisconsin rhyolites. Further, there is no way to determine if the metamorphic events were coeval from available data. The Matlock keratophyre was covered by the Sioux quartzite, which has undergone diagenesis, if not low-grade metamorphism, and the alteration that affected the keratophyre may have been related to this event.

Anderson et al. (1975) and Smith (1978a, b) interpreted the  $1760 \pm 10$  Ma age of the Wisconsin rocks as indicating that they formed during the waning stages of the 1860-1900 Ma Penokean orogeny (Sims and Peterman, 1986). However, Bickford et al. (1986) have proposed that a younger compressional province, the Central Plains orogen, formed approximately 1.75 Ga to the west and possibly to the south of the Superior province. The Matlock keratophyre may have been formed during this orogenesis. The boundary between the proposed Central Plains orogen and the Penokean orogen is unknown. Van Schmus et al. (1989) determined that the  $1433 \pm 4$  Ma Quimby granite, located approximately 80 km south of Matlock, was derived from juvenile Early Proterozoic crust formed approximately 1860 Ma, although they could not establish unequivocally whether this terrane was the southwestern extension of the Penokean orogeny or the eastern extension of the Central Plains orogen.

#### SUMMARY

The Matlock keratophyre is a felsic pyroclastic deposit that has undergone low-grade metamorphism resulting in severe chemical alteration including depletion of LILE and other incompatible elements. In contrast, gabbro xenoliths, derived from the underlying Otter Creek layered igenous complex, were strongly enriched in those elements depleted from the keratophyre. The Matlock keratophyre occupies a stratigraphic position similar to felsic rocks in Wisconsin and the  $1782 \pm 10$  Ma age determined for the Matlock volcanics is essentially the same as the age of  $1760 \pm 10$  Ma obtained by Van Schmus (1978) for the Wisconsin rocks. Rocks from both localities also exhibit evidence of subsequent low-grade metmorphism, although elemental redistribution in the keratophyre was far more extensive than in the Wisconsin samples. It is impossible to determine the timing of the alteration of the keratophyre from available data. The Wisconsin rocks are spatially associated with the approximately 1850 Ma Penokean orogen whereas the Matlock volcanics cannot be unequivocally assigned to either the Penokean province or the proposed 1750 Ma Central Plains orogen.

#### ACKNOWLEDGEMENTS

We acknowledge Mike Peters and Brian Gedlinske for assistance in the thin section and X-ray diffraction study of these samples. Bruce Tanner provided XRF data obtained at Iowa State University. Financial support for this study was provided by Iowa Science Foundation grant ISF-85-8 to KEW and KES for mineralogical and major- and traceelement analyses. INAA studies were made possible by a Department of Energy cost sharing grant to the University of Missouri Research Reactor.

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