STATE OF ILLINOIS

DEPARTMENT OF REGISTRATION AND EDUCATION

Trace Elements, Rare Earths, and Chemical Composition of Southern Illinois Igneous Rocks

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ILLINOIS STATE GEOLOGICAL SURVEY
URBANA

1962 CIRCULAR 330

TRACE ELEMENTS, RARE EARTHS, AND CHEMICAL COMPOSITION OF SOUTHERN ILLINOIS IGNEOUS ROCKS

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ABSTRACT

This investigation was made in order to answer the many questions that have been raised regarding the rare earth, trace element, and general chemical composition of the igneous intrusive rocks of southern Illinois, to determine the present possible commercial significance of these rocks, and to provide data in connection with development of possible future uses. The intrusive rocks occur as dikes, sills, and explosion breccias. Fifteen of the known deposits were sampled. The trace element content and rare earth content of all samples were determined spectrographically; nine samples were analyzed by wet gravimetric methods. A number of samples were fused to determine whether they would produce unusual kinds of glass. The results of the tests failed to show any unusual major compositional characteristics that would suggest special uses for the rocks. The amounts of trace elements and rare earths found are not believed to be within the present commercial range for ores.

INTRODUCTION

Hardin, Pope, Saline, Gallatin, and Williamson Counties in extreme southern Illinois comprise the only part of the state in which igneous rocks crop out or come close to the surface. These rocks occur as intrusive bodies of dark colored igneous rock and explosion breccias (Clegg and Bradbury, 1956). During the search for uranium on Hicks Dome in Hardin County in 1955 and 1956, a deposit of radioactive, silty clay, possibly associated with one of the masses of explosion breccia (Bradbury et al., 1955; Bradbury, 1960; Trace, 1960), was found. However, no

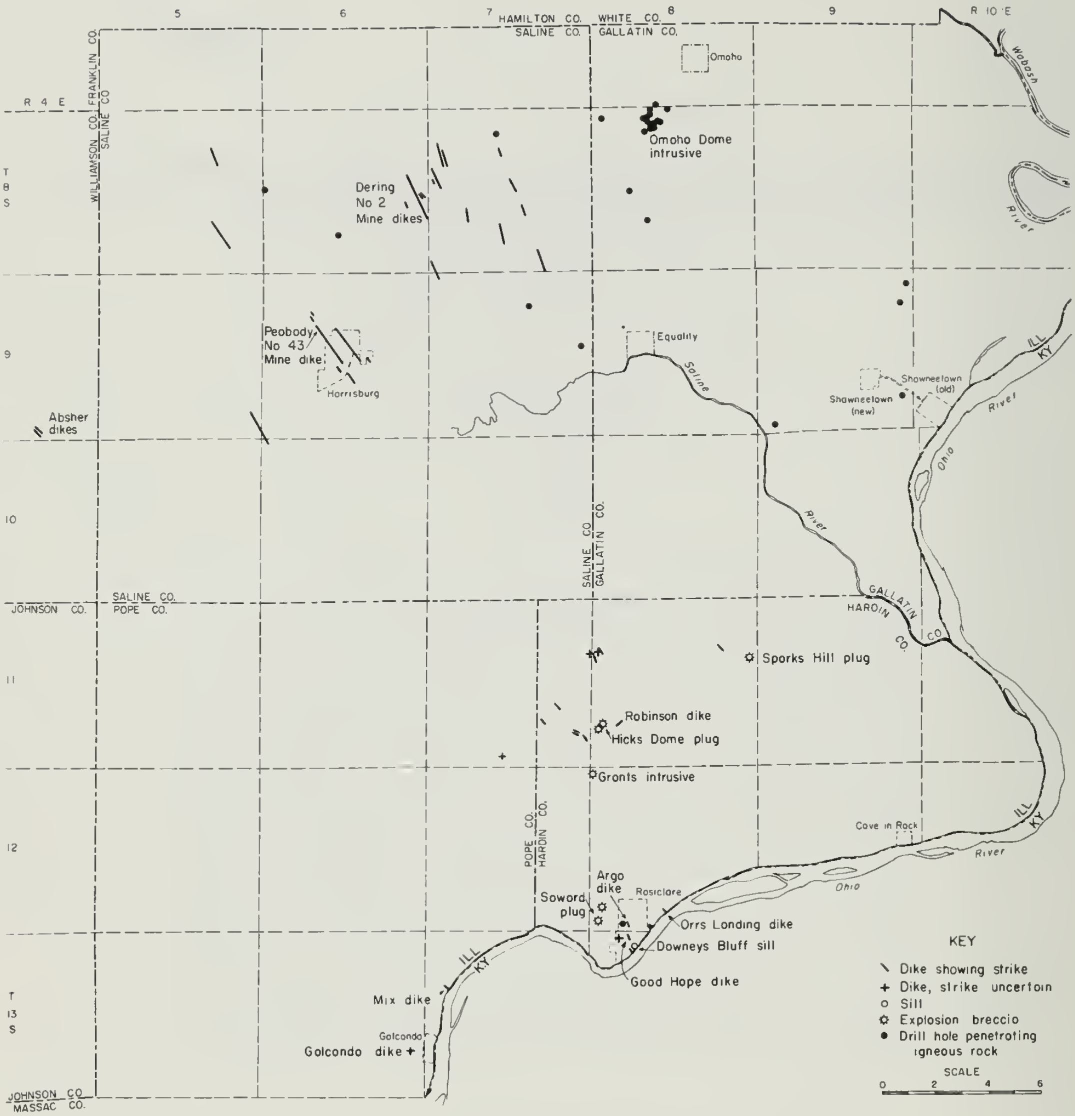

Fig. 1 — Distribution of igneous intrusive rocks in southern Illinois. Some occurrences within city limits of Rosiclare not shown for sake of clarity. (Adapted from Clegg and Bradbury, 1956, plate 1.)

development ensued, presumably because the quantity of the clay was limited. Analyses of three samples of the clay (Bradbury, 1960) showed an average of 3.3 percent total rare earth oxides.

At various times there has been speculation regarding the trace element content of the southern Illinois igneous rocks as well as their general chemical composition and the possibility that they might have special uses. The finding of the radioactive clay, with its abnormal content of rare earths, further increased interest in the intrusives. Figure 1 shows the location of all known igneous intrusive bodies in southern Illinois. Those sampled for analysis are designated by name on the map.

PURPOSE OF INVESTIGATION

This investigation was undertaken to provide data regarding the foregoing matters in order that the present commercial possibilities of the intrusive rocks might be known and that a representative body of data might be available for judging the suitability of these rocks for possible future uses. To this end all major and most minor outcrops of igneous intrusive rocks in Hardin and Pope Counties, three dikes exposed in coal mines in Saline and Williamson Counties, and similar rock from a diamond-drill core from the Omaha Dome in Gallatin County were sampled and analyzed for trace elements and rare earths; major chemical constituents were determined for nine of the samples.

CHARACTER OF DEPOSITS

The intrusive rocks occur as flat or nearly flat-lying sills, vertical or nearly vertical dikes, and plugs. Certain occurrences are referred to simply as "intrusives" because too little is known or can be seen of their shape to permit more specific identification. The dikes may reach a maximum width of 300 feet but generally are less than one to a few feet wide. The sills are rarely more than one foot thick and more commonly are only a few inches thick. The dikes and sills are mica-peridotites or related rocks that have been altered (table 1) by serpentinization, the addition of carbonates (chiefly calcite), or, less commonly, by silicification (Clegg and Bradbury, 1956).

The dimensions of the plugs, which are composed of explosion breccia, are not determinable, but one of them crops out over a 400- by 800-foot area. Alteration of the breccias has been similar to that of the dikes and sills (table 1).

SAMPLES AND RESULTS OF TESTS

Table 1 lists the deposits sampled, their location, the thickness of the rock represented by each sample, the kind of rock composing the sample, its physical appearance, and the character of alteration.

TABLE 1. - SOURCE AND

Sample no.	Name	Location Quarters	Sec.	T.	R.	County	Thickness sampled (ft.)	Kind of rock
1	Downeys Bluff sill	NW NW SE	5	13S	8E	Hardin	2	Lamprophyre?
2	Absher dike	SE SW SE	34	9S	4E	Williamson	9	Mica-peridotite
3	Argo dike	— NE SW	32	12S	8E	Hardin	2	Lamprophyre?
4	Dering #2 dike	— SE NE	24	8S	6E	Saline	15	Mica-peridotite
5	Golconda dike	NW SW NE	25	13S	6E	Pope	—	Mica-peridotite
6	Good Hope dike	— NE NW	5	13S	8E	Hardin	1	Lamprophyre?
7	Mix dike	— NE NE	18	13S	7E	Pope	15	Mica-peridotite
8	Orrs Landing dike	NE SW NE	33	12S	8E	Hardin	1	Lamprophyre?
9	Peabody #43 dike	— SE NE	17	9S	6E	Saline	6	Mica-peridotite
10	Robinson dike	NW SW NW	29	11S	8E	Hardin	2±	Mica-peridotite?
11	Omaha Dome intrusive	SE NW SW	4	8S	8E	Gallatin	11½	Mica-peridotite
12	Hicks Dome plug	SE SE NW	30	11S	8E	Hardin	(*)	Explosion breccia
13	Grants intrusive	SE NW NW	6	12S	8E	Hardin	5	Explosion breccia
14	Soward plug	— NE SW	31	12S	8E	Hardin	(†)	Explosion breccia
15	Soward plug	— NE SW	31	12S	8E	Hardin	(†)	Explosion breccia
16	Sparks Hill plug	SW NE NE	13	11S	8E	Hardin	(⁂)	Explosion breccia

* Samples from boulders and ledges on the west half of small hill.

† Samples taken from a 400 by 800 foot outcrop area.

⁂ Samples taken from creek bed at intervals for a distance of 300 feet.

CHARACTER OF SAMPLES

Color	Texture	Type of alteration	Comments
Dark greenish gray	Fine grained	Abundant carbonate	———
Dark greenish gray	Medium grained	Partial serpentinization	In coal strip mine
Gray	Fine grained	Mostly carbonate	At 500-ft. level in Argo mine
Dark greenish gray	Fine grained	Serpentinization	Dike in coal mine
Dark greenish gray	Medium grained	Serpentinization	Sample from boulders
Greenish gray	Fine grained	Silicification	In Good Hope mine
Dark greenish gray	Coarse grained	Partial serpentinization	In bluff along railroad; boulders
Dark gray	Fine grained	Mostly carbonate	———
Dark greenish gray	Fine grained	Carbonate; serpentinization	Dike in Peabody 43 coal mine
Brown	Coarse grained	———	Weathered rock in pit
Dark greenish gray	Fine grained	Serpentinization	Sample from diamond drill core
Brown	Matrix fine grained	Silicification	———
Greenish gray	Matrix fine grained	Abundant carbonate	———
Gray	Matrix fine grained	———	Unweathered
Brown	Matrix fine grained	Oxidized	Weathered
Dark gray	Matrix fine grained	Abundant carbonate	———

Table 2 gives the results of wet gravimetric chemical analyses for nine samples and indicates the major chemical constituents of these samples; table 3 reports on trace element content and table 4 on rare earths.

DISCUSSION OF DATA

Major Chemical Constituents

The nine samples in table 2 show a great diversity of composition. Sample 12, Hicks Dome plug, contains the greatest amount of silica, a moderate amount of alumina, and very little of the other compounds listed. The high silica content is related to the fact that the rock is composed chiefly of chert fragments in a fine-grained quartz cement (Bradbury et al., 1955, p. 7, sample 50 (125); Clegg and Bradbury, 1956, p. 17, table 1, occurrence (1)).

Sample 8, Orrs Landing dike, is high in carbonates; also containing important amounts of carbonates are samples 1, 14, and 16. The carbon dioxide reported in these samples, if calculated to calcium carbonate, yields the figures given below:

Sample	Calculated $CaCO_3$
1	41.5%
8	86.5%
14	34.6%
16	41.8%

Petrographic examination of these four rocks reveals that the mineral calcite ($CaCO_3$) has replaced considerable proportions of the original mineral constituents (Clegg and Bradbury, 1956, p. 13-15 and table 1).

Sample 10, Robinson dike, is unusual in its comparatively high content of alumina, ferric oxide, and phosphorous pentoxide. As the Robinson dike was extremely weathered, it is probable that these three oxides are residual concentrations, with the alumina and ferric oxide occurring in the weathering products clay and limonite, respectively, and the phosphorous in apatite, a common accessory mineral in the mica-peridotites and one that is highly resistant to weathering. Also high in total iron ($Fe_2O_3 + FeO$) are samples 1, 2, 7, and 11.

Sample 1, Downeys Bluff sill, and samples 14 and 16, Soward and Sparks Hill breccia plugs, contain higher than average amounts of soda (Na_2O). In samples 14 and 16 the soda probably is contained in plagioclase, An_{15}, which has been recognized in thin sections of these rocks. No sodium minerals could be positively identified in thin sections of the Downeys Bluff sill, but an X-ray diffractogram revealed the presence of analcite, a sodium aluminum silicate ($NaAlSi_2O_6 \cdot H_2O$).

As no feldspar or feldspathoids have ever been reported from thin section studies of the sill and dike rocks of southern Illinois (Clegg and Bradbury, 1956; Weller et al., 1952; Currier, 1920; Johannsen, 1905), the analcite in the Downeys Bluff sill is the first concrete evidence that some of the dike rocks originally contained feldspathic minerals. Johannsen (1905) was the first to suggest that the more extensively altered dikes, particularly those that were replaced in large part by carbonate, originally may have contained feldspar and no olivine and should, therefore, be classed as lamprophyres. The Orrs Landing dike (sample 8), which is two-thirds carbonate, may be a lamprophyre that was depleted in soda through extensive replacement of the rock by carbonate. The other dike rocks in table 2, with the exception of the highly weathered Robinson dike, are undoubted mica-peridotites.

The potash raises no such problems as the soda. Phlogopite, a potassium-magnesium mica, in the sill and dike rocks and potash feldspar in the plug rocks appear to be the sources of the potash.

Titania (TiO_2) is present in concentrations of over 4 percent in three of the nine samples and of over 5 percent in two samples. Examination of thin sections of the rocks revealed that most of the titania is contained in the mineral perovskite ($CaTiO_3$) in fresh peridotite, and in leucoxene (chiefly TiO_2, an alteration product of titanium minerals) in altered rock. Grain sizes of the titanium minerals were typically 0.5 mm for perovskite and 0.1 to 0.2 mm for leucoxene. Although it is conceivable that such relatively low concentrations might be commercial in some deposits, the fine grain size of the titanium minerals in the southern Illinois intrusives would make their recovery difficult and their profitable production questionable.

No specific uses for the samples tested are recognized on the basis of the chemical analyses although it is possible that some of the samples might meet the requirements for some special purpose.

The possibility that some of the samples might be used for making a variety of glass was explored by fusion tests. Three samples of explosion breccia and two samples of mica-peridotite, representing bodies of rock of possible minable size, were powdered and heated to 1500° C in a muffle furnace. After cooling, it was found that two of the explosion breccia samples, Sparks Hill and Soward plugs, had yielded a dark greenish glass, although the Sparks Hill sample showed a thin rind of crystalline material next to the crucible wall. The third explosion breccia sample, Hicks Dome plug, had not fused because of its high silica content, 88 percent (table 2). The two samples of peridotite, Mix and Absher dikes, had fused but on cooling had reverted to the crystalline state.

These results can be attributed to the chemical compositions of the rocks involved (table 2). The glass-making properties of a silicate mixture depend, to a large extent, on its content of silica (SiO_2) and alumina (Al_2O_3) (J. S. Machin, personal communication). If the sum of $SiO_2 + Al_2O_3$ falls below about 48 percent, the mixture is not likely to yield a glass. For example, the Soward plug rock, which had fused entirely to glass, contains 55.6 percent $SiO_2 + Al_2O_3$. The Sparks Hill plug sample, with 49.3 percent $SiO_2 + Al_2O_3$, just above the prescribed minimum, yielded mostly glass. The Absher and Mix dikes, containing less than 48 percent $SiO_2 + Al_2O_3$, did not yield a glass.

Trace Elements

The trace element data in table 3 indicate that none of the elements reported upon occur in amounts exceeding .2 percent, most of them occurring in smaller or very much smaller amounts. No uses for the intrusive rocks are recognized on the basis of their trace element content.

Rare Earths

The rare earth content of all samples tested was less than .2 percent (2000 parts per million), with the exception of sample 8 which contained .21 percent (table 4). Samples 9, 10, and 14 contained no rare earths in amounts detectable by the spectrographic procedures used. Samples 5, 11, 12, and 15 contained very little rare earths. Sample 8, Orrs Landing dike, and sample 13, Grants intrusive, contained the largest amounts of rare earths.

Igneous rocks such as those described herewith are not common commercial sources of rare earths, and insofar as is known the amounts of rare earths found in the southern Illinois igneous rocks are not sufficiently great to place them in the category of ores at the present time. Because of the infancy of the rare earth industry, the experimental nature of ore processing methods, and the lack of an established market for rare earth metals, industry-wide specifications for ores or concentrates do not exist (Whitman, 1960). However, it would appear from the slight amount of information available on grades of ore presently being mined that a commercial deposit should contain several percent rare earth oxides. For example, a bastnaesite deposit at Mountain Pass, California, has an average grade of 10 percent rare earth oxides (Vickery, 1960), and a monazite vein deposit in South Africa contains 35 to 40 percent rare earth oxides (Kremers, 1958).

TABLE 2. - CHEMICAL ANALYSES OF IGNEOUS ROCKS

(Analyses by L. D. McVicker)

Sample no.	Source of sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2	Ignition loss	Total
1	Downeys Bluff sill	24.73	2.91	7.43	3.24	7.40	5.98	22.05	2.66	0.89	0.96	18.24	19.59	97.84*
2	Absher dike	31.88	2.88	8.37	8.80	3.30	17.34	17.01	0.08	0.83	0.87	0.52	7.97	99.33*
7	Mix dike	33.34	4.12	5.31	7.78	4.82	22.91	10.38	0.27	1.75	0.39	2.52	9.32	100.39
8	Orrs Landing dike	4.71	0.52	2.60	0.62	3.91	7.27	38.26	0.06	0.36	1.64	38.04	37.83	97.78*
10	Robinson dike	33.93	5.56	11.62	20.94	0.29	7.72	5.65	0.46	1.22	3.65	0.25	7.90	98.94*
11	Omaha Dome intrusive	28.61	5.06	5.88	8.84	5.23	17.96	13.75	0.33	2.41	0.42	6.07	10.32	98.81*
12	Hicks Dome plug	87.82	0.21	6.31	0.95	0.10	0.12	0.07	0.04	0.47	0.06	0.00	1.62	97.77*
14	Soward plug	45.83	1.08	9.74	0.76	4.66	3.64	12.60	4.49	0.85	0.51	15.39	16.31	100.47
16	Sparks Hill plug	40.14	1.16	9.14	1.08	5.17	5.64	13.49	2.44	1.40	0.52	18.40	19.32	99.50

* May contain small amounts of a few, undetermined constituents.

TABLE 3. - SEMIQUANTITATIVE ANALYSES OF TRACE ELEMENTS FOUND IN IGNEOUS ROCKS
(Percent by weight)

(Analyses by Kozo Nagashima)

Sample no.	Source of sample	Sr	Co	Ni	Zr	Ag	V	Be	Pb	Cr	Mn
1	Downeys Bluff sill	.1	.002-.001	.001	.02	.0001	.02-.01	.003	.004	nd†	.1
2	Absher dike	.05	.005	.05-.02	.02	.0001	.01	nd	.004	.02	.1
3	Argo dike	.1-.05	.001	.002-.001	.02	.0001	.01	nd	.004	nd	.1
4	Dering #2 dike	.05	.005-.002	.05-.02	.01	nd	.01-.005	nd	nd	.05	.1
5	Golconda dike	.1-.05	.002	.02	.02	nd	.01-.005	nd	.002	.05-.02	.1
6	Good Hope dike	.05-.02	nd	.001	.06-.03	.001-.0005	.01	nd	.1	nd	.01
7	Mix dike	.05	.005	.05-.02	.01	nd	.01-.005	nd	nd	.05-.02	.1
8	Orrs Landing dike	.02-.01	nd	nd	.03	.0001	.005	nd	.004	nd	.1
9	Peabody #43 dike	.05	.005-.002	.002	.01	nd	.01	nd	.004	.05-.02	.1
10	Robinson dike	.1-.05	.002	.02-.01	.03	.001	.01	.006	.004	.02	.1
11	Omaha Dome intrusive	.1-.05	.005-.002	.02	.02	nd	.01-.005	nd	.004	.02	.1
12	Hicks Dome plug	.1-.05	.01-.005	nd	.03-.02	nd	.005	nd	.002	.01	.01
13	Grants intrusive	.2-.1	.005-.002	.005-.002	.02	.0001	.01	.0006	.002	.02-.01	.1
14	Soward plug	.2-.1	.001	.002-.001	.03	nd	.01	.0006	.004	nd	.1
15	Soward plug	.2-.1	nd	.002-.001	.02	nd	.01-.005	.0006	.006	nd	.1
16	Sparks Hill plug	.2-.1	.002-.001	.002-.001	.02	.0001	.01-.005	.0003	.002	nd	.1

Elements sought but not detected (limits of detection are in parentheses): Mo (0.001%), Ge (0.001%), Sn (0.001%), Cd (0.01%), Sb (0.01%), Zn (0.02%), Tl (0.01%), As (0.04%), Ga (0.01%), Nb (0.01%), and Bi (0.001%). Copper was detected in all samples but estimation of amount was impossible because of high blank.

† nd - not detected.

TABLE 4. - RARE EARTHS IN IGNEOUS ROCKS
(parts per million*)

(Analyses by Juanita Witters)

Sample no.	Source of sample	CeO_2	Dy_2O_3	Er_2O_3	Gd_2O_3	Ho_2O_3	La_2O_3	Nd_2O_3	Pr_6O_{11}	Yb_2O_3	Y_2O_3
1	Downeys Bluff sill	100	Tr	nd†	nd	nd	100	100	Tr	0.2	30
2	Absher dike	100	nd	nd	30	nd	80	100	Tr	0.05	50
3	Argo dike	200	Tr	10	100	3	400	100	Tr	0.2	200
4	Dering #2 dike	200	20	10	40	nd	270	400	100	0.3	150
5	Golconda dike	nd	nd	nd	nd	nd	80	nd	nd	nd	nd
6	Good Hope dike	200	30	6	30	nd	330	300	50	0.1	90
7	Mix dike	100	nd	Tr	20	nd	30	Tr	nd	Tr	Tr
8	Orrs Landing dike	800	10	30	200	6	300	300	50	2.0	400
9	Peabody #43 dike	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	Robinson dike	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	Omaha Dome intrusive	nd	nd	Tr	nd	nd	10	nd	nd	nd	nd
12	Hicks Dome plug	nd	nd	Tr	nd	nd	nd	nd	nd	0.4	20
13	Grants intrusive	400	5	nd	100	5	330	400	20	0.1	100
14	Soward plug	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
15	Soward plug	nd	nd	nd	nd	nd	20	nd	nd	Tr	Tr
16	Sparks Hill plug	300	nd	8	20	nd	260	200	50	0.09	80
Limits of detection**		100	5	5	20	2	10	50	20	0.05	20

Uncertainty is estimated to be ½x - 2x. Due to agreement with published results for La, Nd, and Y in Standard Granite G-1, and rational totals for samples not included in this report, dependent chiefly on Ce, La, and Y, the second significant figure has been retained for La and Y to reflect a possible 20 percent uncertainty.

* 1000 parts per million equals 0.1 percent.
† nd - not detected; less than the indicated limit of detection.
** Using the rare earth concentrate from 2 grams of sample collected in 100 mg CuO.

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Illinois State Geological Survey Circular 330
12 p., 1 fig., 4 tables, 1962

Printed by Authority of State of Illinois, Ch. 127, IRS, Par. 58.25.

CIRCULAR 330

ILLINOIS STATE GEOLOGICAL SURVEY

URBANA

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