

# Proceedings of the 47th Forum on the Geology of Industrial Minerals



*Thornton Quarry (photograph by Donald Mikulic)*

## Rare Earth Mineral Concentrations in Ultramafic Alkaline Rocks and Fluorite Within the Illinois-Kentucky Fluorite District: Hicks Dome Cryptoexplosive Complex, Southeast Illinois and Northwest Kentucky (USA)

F.B. Denny,<sup>1</sup> R.N. Guillemette,<sup>2</sup> and L. Lefticariu<sup>3</sup>

<sup>1</sup>Illinois State Geological Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign

<sup>2</sup>Department of Geology, Texas A&M University, College Station, Texas

<sup>3</sup>Department of Geology, Southern Illinois University, Carbondale, Illinois

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### ILLINOIS STATE GEOLOGICAL SURVEY

Prairie Research Institute

University of Illinois at Urbana-Champaign

615 E. Peabody Drive

Champaign, Illinois 61820-6918

<http://www.isgs.illinois.edu>



# Rare Earth Mineral Concentrations in Ultramafic Alkaline Rocks and Fluorite Within the Illinois-Kentucky Fluorite District: Hicks Dome Cryptoexplosive Complex, Southeast Illinois and Northwest Kentucky (USA)

**F.B. Denny\***

*Illinois State Geological Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign*

**R.N. Guillemette**

*Department of Geology, Texas A&M University, College Station, Texas*

**L. Lefticariu**

*Department of Geology, Southern Illinois University, Carbondale, Illinois*

## ABSTRACT

The rare earth elements (REE) are composed of the Lanthanide Series of 15 elements with atomic numbers (57) through (71) and yttrium (39). Because of their geochemical behavior, REE rarely form their own minerals and more commonly are found incorporated within the structure of other minerals. There is growing concern over the economical availability of REE because of their diverse and expanding array of technological applications and limited supply. This paper presents the results of a mineralogical and geochemical study of fluorite ore, ultramafic rock, and igneous breccia from the Illinois-Kentucky Fluorite District (United States). Igneous rocks and fluorite ore were analyzed through whole-rock trace element geochemistry and electron microscopy to determine the relative abundance of REE. Geochemical analysis (inductively coupled plasma atomic emission spectroscopy and inductively coupled plasma mass spectrometry) from outcrop samples at the Sparks Hill Diatreme (Hardin County, Illinois) detected elevated concentrations of cerium group or light REE: lanthanum (La, 293 ppm), cerium (Ce, 467 ppm), praseodymium (Pr, 45.5 ppm), and

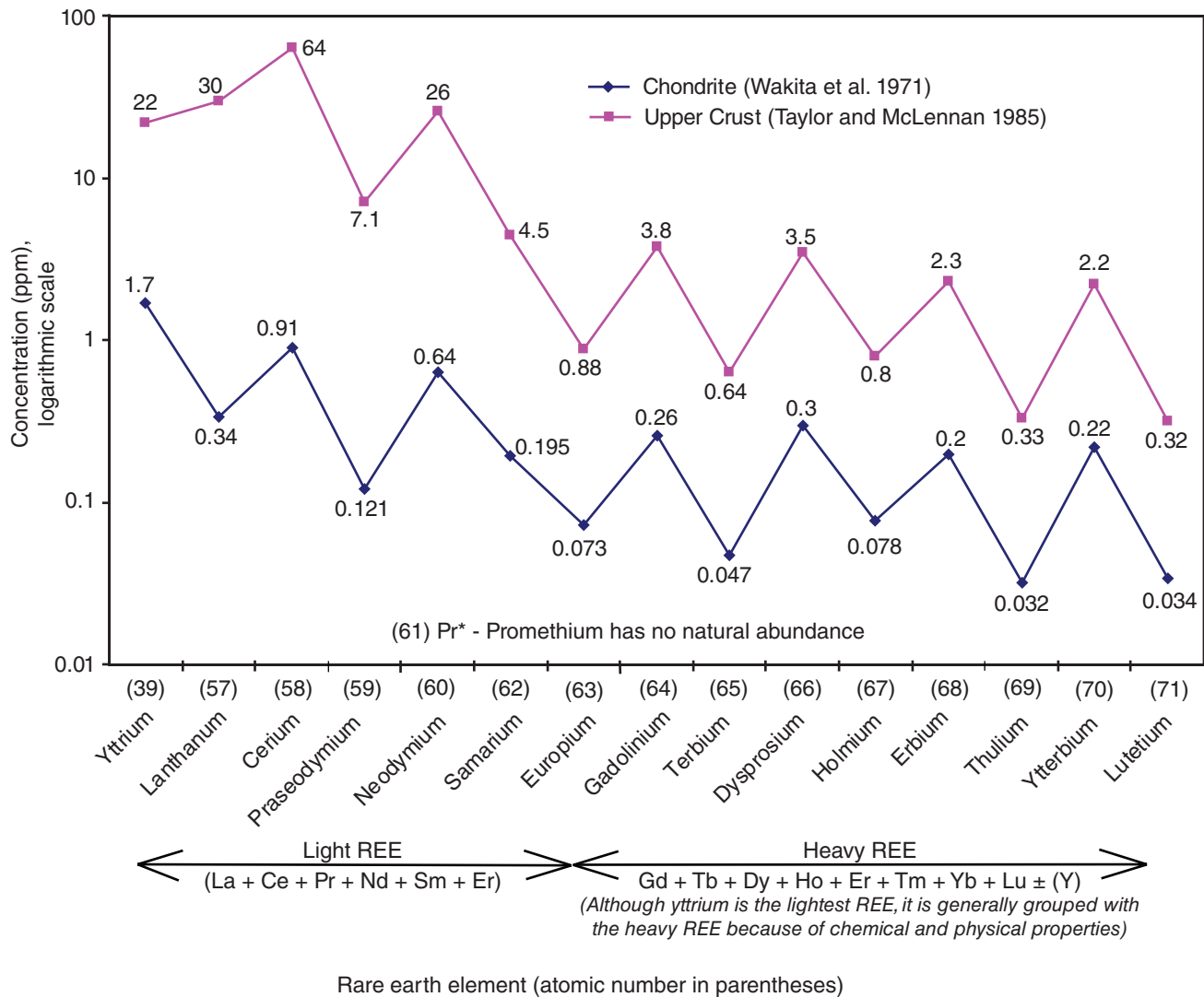
neodymium (Nd, 143 ppm). Results of electron microprobe analyses indicate that the source of REE anomalies in the Sparks Hill Diatreme is an REE fluorocarbonate mineral. Electron microscopy detected several tabular fluorocarbonate grains that are less than 20  $\mu\text{m}$  in size and associated with an unidentified aluminum-strontium (Al-Sr) phosphate. The fluorocarbonate was identified as synchysite  $[\text{Ca}(\text{Ce}, \text{La}, \text{Nd}, \text{Y})(\text{CO}_3)_2\text{F}]$  and was found in both the well-rounded clasts and the matrix within the diatreme/breccia. Synchysite is similar to other rare earth fluorocarbonates, such as parisite  $[\text{Ca}(\text{Ce}, \text{La}, \text{Nd})(\text{CO}_3)_2\text{F}]$ , bastnasite  $[(\text{Ce}, \text{La}, \text{Y})\text{CO}_3\text{F}]$ , and rontgenite  $[\text{Ca}(\text{Ce}, \text{La})(\text{CO}_3)_2\text{F}]$ . These fluorocarbonate minerals can occur together as intergrowths and thus are difficult to distinguish. The identification of a rare earth fluorocarbonate mineral within the igneous diatreme/breccia at Sparks Hill can have significant economic implications relating to the concentration of REE within the Illinois-Kentucky Fluorite District. Future studies will focus on the fluorite, igneous breccia, and rare earth fluorocarbonate through additional geochemical and electron microprobe analyses.

## RELEVANCE OF THE STUDY

In 2010, as part of an Illinois state-wide geologic mapping program (STATEMAP), a geochemical analysis of an igneous breccia detected 293 ppm of lanthanum and 467 ppm of cerium (Denny et al. 2010). The rare earth element (REE) values within this sample were elevated, and an effort was undertaken to identify the source of the REE. The igneous breccia "Sparks Hill Diatreme" is located within the Illinois-Kentucky Fluorite District (IKFD) approximately 5 mi (8 km) northwest of Hicks Dome. Although the IKFD has been examined and studied for many years, few geologic investigations have been focused on determining the concentrations of REE within the ultramafic igneous rocks, igneous breccia, and fluorite bodies of this district. This paper presents geochemical and electron microprobe results of REE and other trace elements from fluorite ore and igneous rocks associated with Hicks Dome in southeastern Illinois. These data are preliminary, but because of the apparent elevated REE values and the present interest in these elements, the preliminary results are presented to focus future research and mineral exploration efforts. The authors are continuing to investigate these rocks and ideally will provide additional quantitative analyses.

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\*Corresponding author: [fdenny@illinois.edu](mailto:fdenny@illinois.edu).



**Figure 1** Graphical representation of the average concentrations of rare earth elements (REE) in the upper crust from Taylor and McLennan (1985) and the average concentrations of REE in chondrite or “stoney” meteorites from Wakita et al. (1971).

## INTRODUCTION TO RARE EARTH ELEMENTS

Rare earth elements are becoming increasingly important for high-technology applications because of their physical and chemical nature. These “high-tech” elements are being utilized in various military systems, making such elements important to the defense of the United States. Locating REE resources within the United States will be critical to the strategic defense of the United States and for the economic viability of emerging technologies that rely on these resources. Economic concentrations of

rare earth minerals have been detected worldwide in association with alkaline igneous activity, carbonatite systems, coastal placers, and hydrothermal systems. Long et al. (2010) provided an updated review of all known REE deposits within the United States and cited Hicks Dome in Illinois as a potential economic resource.

The REE are yttrium (atomic number 39) and the lanthanides, which are 15 elements from lanthanum (57) to lutetium (71) (Henderson 1996). In general, the larger the atomic number, the smaller the concentration of the particular REE

within the upper portion of the earth’s upper crust. The REE are generally subdivided based on their atomic numbers. The light REE (LREE), also called the “cerium group,” include lanthanum (57) to europium (63). The heavy REE (HREE) include gadolinium (64) to lutetium (71) and are called the “yttrium group.” Although yttrium is not normally considered an HREE, it is usually grouped with the HREE because of their chemical and physical similarities. The estimated average abundance of REE for the upper continental crust is given graphically in Figure 1. Promethium (61), a highly radioactive element with a short half-

life, exists only as a temporary intermediate product in the decay of other radioactive elements and is omitted from REE data sets. The graphical representation of these data sets exhibits an obvious “high-low” oscillation, which stems from even-atomic-numbered REE having a greater relative stability of the nuclei as compared with odd-atomic-numbered REE. This oscillation is referred to as the Oddo–Harkins effect (Henderson 1996). To normalize and smooth the data, graphical representations are normalized by using chondritic REE concentrations and plotted on a logarithmic scale.

Rare earth elements have been reported to occur within halides such as fluorite, fluorocarbonates, oxides, phosphates, silicates, iron ore, and other chemical forms. In silicate melt systems, the large ionic size of the rare earth ions precludes their entry into most minerals to any significant extent. Therefore, the concentration of REE tends to be concentrated in the melt and may become increasingly concentrated through fractional crystallization (Henderson 1996). Certain minerals in basic igneous melts will readily accept the REE into their structure, such as garnet, apatite, fluorite, titanite, and perovskite, but normally only at concentrations of a few percent. Additionally, REE are not easily concentrated and are relatively immobile through most natural processes.

## REGIONAL GEOLOGY OF THE STUDY AREA

The study area is located at the southern end of the Illinois Basin in extreme southeastern Illinois. Lower to Middle Pennsylvanian sandstone, shale, and coal dip gently at two to three degrees northerly into the basin. Upper Mississippian rocks are present beneath a regional Pennsylvanian-Mississippian unconformity. These Mississippian (Chesterian Series) units are composed of alternating layers of limestone, sandstone, and shale and grade downward into a relatively siliciclastic-free Lower Mississippian (Valmeyeran Series) limestone and dolostone sequence. The lowermost Mississippian units are composed of dark gray to black shale of the New Albany Group, which extends

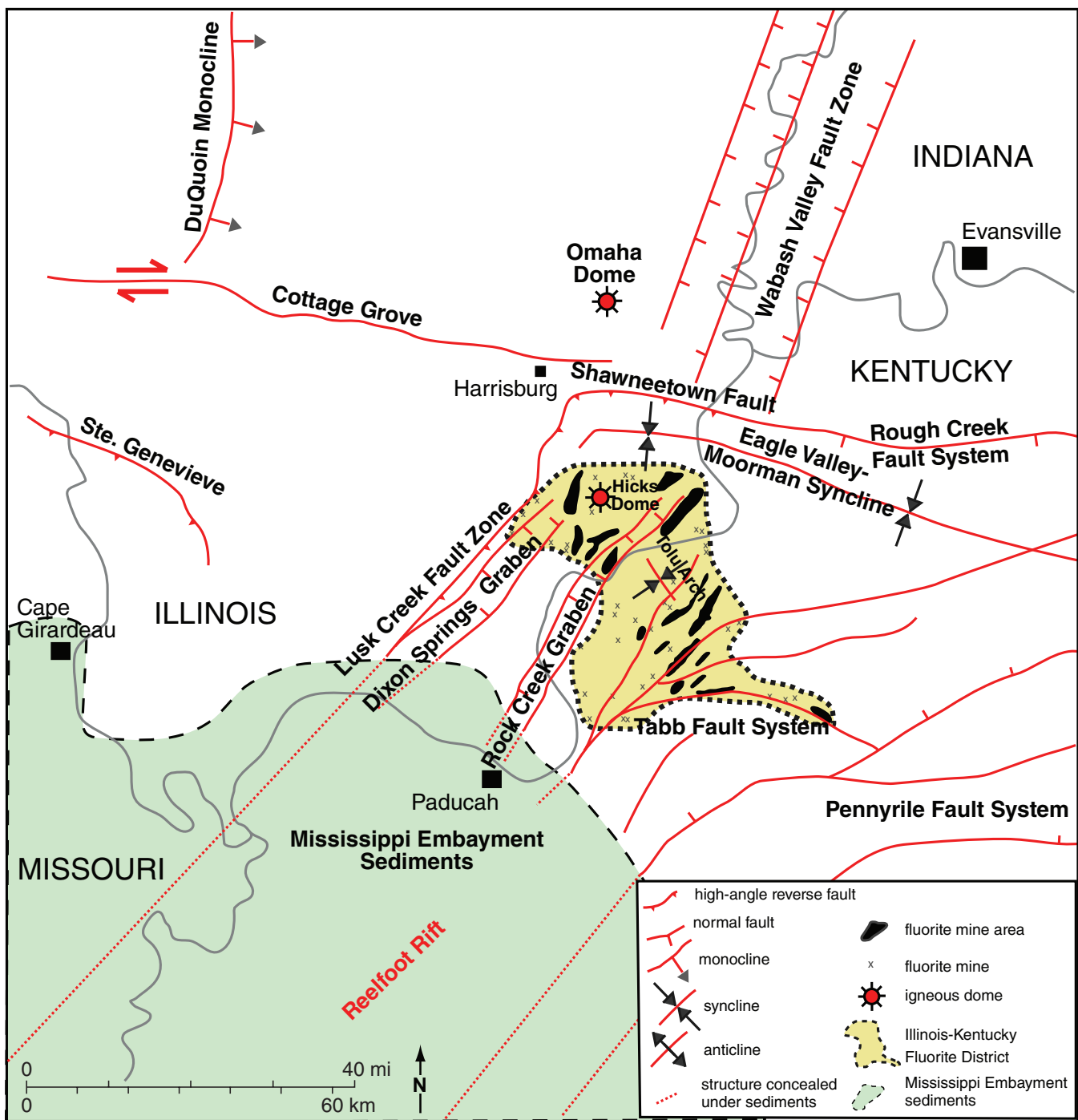
into the Upper Devonian. Below the New Albany Shale, silicified limestone and dolomite of the Middle Devonian are present. Complicating these stratigraphic sequences are Permian Age ultramafic intrusions, diatremes, dikes, and sills, which have created domes and a regional structural arch. A broad regional arch uplifts the Mississippian strata along the Ohio River in southeastern Illinois and northwestern Kentucky. The regional arch is named the Kutawa (Heyl et al. 1965) or Tolu (Bradbury and Baxter 1992), and igneous dikes and sills and igneous breccia are documented along its axis from Kentucky and into southeastern Illinois. Hicks Dome lies approximately in the center of this regional igneous complex in northwestern Hardin County, Illinois (Figure 2). Hicks Dome is mapped as a crudely shaped oval that is elongated in a northwest–southeast direction. Lower to Middle Devonian sedimentary rocks outcrop at the center with younger Lower Mississippian rocks, dipping away from the center of the oval dome (Figure 3). Concentric and radial faults are present along with younger northeast-trending normal faults, which offset the structural fabric of the dome. Baxter and Desborough (1965) estimated vertical uplift on sedimentary units at Hicks Dome to be 4,000 ft (1,200 m) and the diameter of the uplift to be 10 mi (16 km). Previous authors have commonly referred to the feature as cryptovolcanic, but Hicks Dome is properly termed a cryptoexplosion feature because no associated volcanic extrusive rock is documented in the region (Nelson 1995). Explosive autolithic breccia pipes and diatremes are present in several localities along the axis of the igneous complex, and the explosive activity was recognized by Brown et al. (1954). These igneous rocks contain magnetite and can usually be modeled through geophysical techniques. The Coefield Magnetic Anomaly (Hildenbrand et al. 1995) and several additional magnetic anomalies were delineated through gravity and magnetic geophysical techniques. These magnetic anomalies were interpreted by Hildenbrand et al. (1995) as being related to postreactivation along the Wabash Valley Fault Zone along the northern margin of the Reelfoot Rift. Additionally, several periods of struc-

tural deformation occurred in the area, and this region has been called the most complexly faulted zone in the North American Midcontinent (Nelson 1995).

## ILLINOIS-KENTUCKY FLUORITE DISTRICT

Over 7 million tons of fluorite have been mined from the IKFD during the last 170 years (Goldstein and Williams 2008). At present, no substantial fluorite production is occurring within the United States. The ore within the IKFD is predominantly fluorite, with lesser amounts of sphalerite, barite, and galena. Although fluorite is predominant, some bedding replacement deposits carry 15% sphalerite, and some sphalerite concentrates are reported to contain 1% cadmium (Trace 1974). Fluid inclusions in fluorite showed that the main stage ore fluid temperature was 140 to 153°C (Richardson and Pinckney 1984), and some exhibited annealing temperatures well below 100°C. Several documented attempts have been made to date the age of the fluorite mineralization. Symons (1994) proposed a late Jurassic date of fluorite mineralization based on paleomagnetic analysis of the host rocks. Chesley et al. (1994) reported an early Permian date [ $277 \pm 16$  million years (Ma)] by using a samarium-147/neodymium-144 ( $^{147}\text{Sm}/^{144}\text{Nd}$ ) isochron for fluorite. Ruiz et al. (1988), using strontium isotope data, reported an early Jurassic date. Harder, in 1987 (as cited in Symons 1994), reported an age date that straddled the Jurassic-Cretaceous boundary ( $135.7 \pm 4.5$  Ma and  $140.6 \pm 4.7$  Ma) based on fission track techniques on fluorite. Brannon et al. (1996) reported a lower Jurassic date (195 Ma) when using uranium-lead (U-Pb) and thorium-lead (Th-Pb) on ore-stage calcite.

These deposits have been classified as Mississippi Valley-type (MVT) because of the ore minerals; their strata-bound nature; and the temperature of formation, salinities of ore fluids, and other geochemical factors (Heyl et al. 1974). The spatial orientation of the IKFD and the Tolu Arch suggests a genetic relationship between the Permian ultramafic activity and the fluorite mineralization within the IKFD. Mineralization within the IKFD probably resulted from

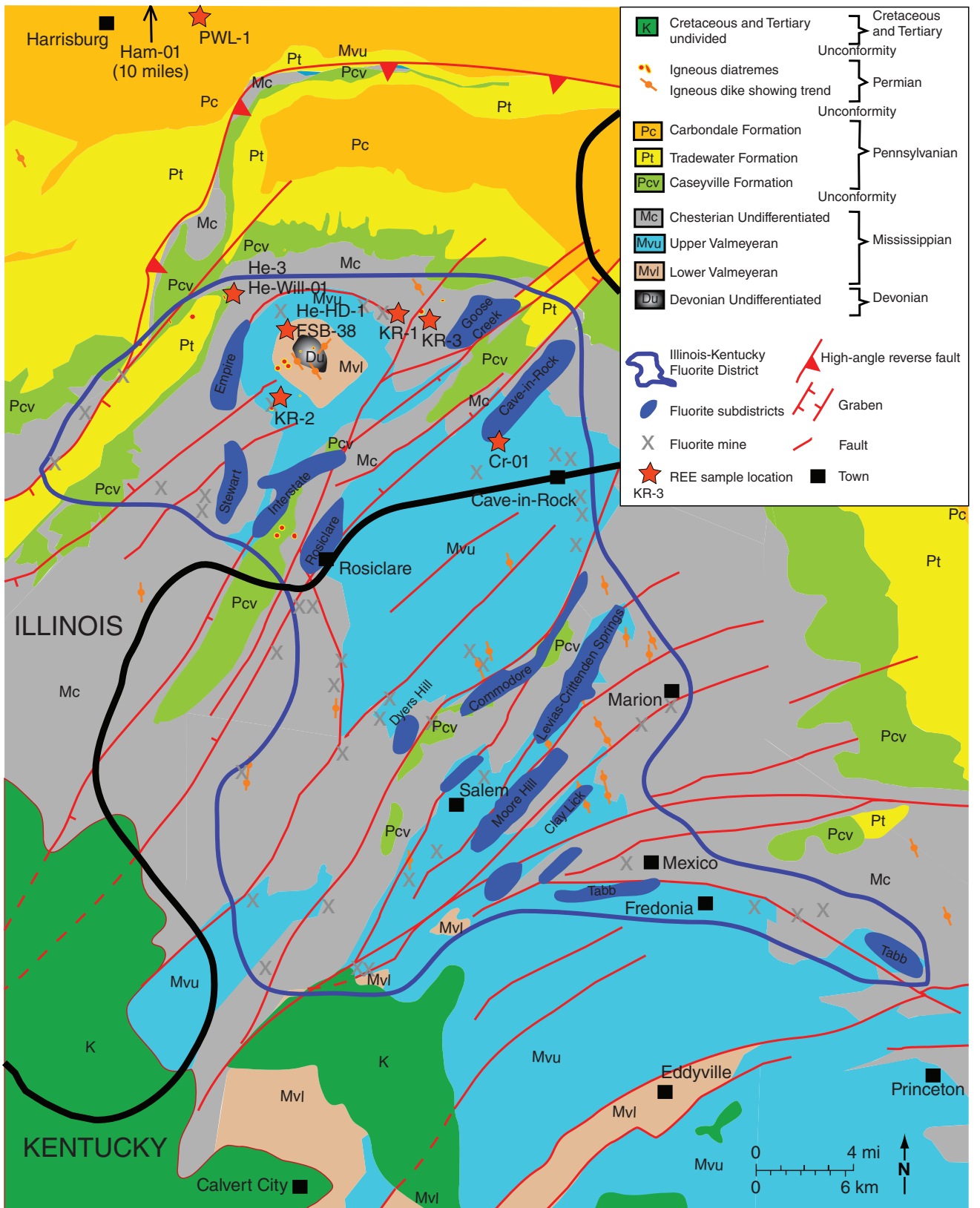


**Figure 2** Location of the Illinois-Kentucky Fluorite District, southern Illinois and northwestern Kentucky, and regional tectonics of the study area (adapted from Denny et al. 2008).

an acidic brine fluid that was charged with fluorine and carbon dioxide (CO<sub>2</sub>)-rich gases produced through degassing of the regional alkaline igneous activity (Plumlee et al. 1995). Although the IKFD has been described as an MVT deposit,

it is an unusual example of this classification because of numerous vein-type mineral deposits and the association of an underlying regional igneous event. Mineralization within the IKFD is probably best described as a fluoritic subtype

of an MVT and may be classified as epithermal. Although the igneous intrusions may not have been important as a heat source, they probably supplied the fluorine for the MVT ore solutions.



**Figure 3** Geology of the study area and the location of the REE samples (adapted from Denny et al. 2008).

## REGIONAL IGNEOUS ACTIVITY

### Radiometric Age Determinations of Igneous Rocks in the Study Area

Reynolds et al. (1997) reported radiometric argon-40/argon-39 ( $^{40}\text{Ar}/^{39}\text{Ar}$ ) age dates of  $272.7 \pm 0.7$  Ma for the Grant intrusive breccia (Hardin County, Illinois). Fifarek et al. (2001) reported the  $^{40}\text{Ar}/^{39}\text{Ar}$  radiometric age determinations on phlogopite from the Davenport Mine Dike (Kentucky) as  $271.0 \pm 0.3$  Ma and the Hutson Mine Dike (Kentucky) as  $267.8 \pm 1.3$  Ma, and they suggested the igneous activity along the Tolu Arch was probably related to extension of the North American plate during the Permian through partial melting of the upper mantle. Radiometric  $^{40}\text{Ar}/^{39}\text{Ar}$  age determinations on phlogopite from the Cottage Grove Dike (Saline County, Illinois) yielded an apparent age of  $269.61 \pm 0.39$  Ma (Denny 2005).

### Previous Geochemical Analyses and Studies of Igneous Rocks in the Study Area

Currier (as cited in Weller 1920) described three types of igneous rocks in the region: Type 1, fine-grained, dark-colored “trap” or lamprophyre; Type 2, medium-grained, dark-colored, mica-peridotite; and Type 3, volcanic breccia. The author stated that all three types are highly altered, making precise identification difficult. The lamprophyre (Type 1) is composed of phlogopite, pyroxene altered to serpentine, and apatite, all encased in a matrix of secondary calcite. The mica peridotite (Type 2) is composed of olivine and pyroxene crystals largely altered to serpentine, phlogopite, iron oxides, and obscure alteration products. The volcanic breccia (Type 3) is composed of angular to rounded igneous and sedimentary rock, fragments of feldspar, quartz, and abundant alteration material.

Brown et al. (1954) studied drill core from Hicks Dome and described the igneous breccia as explosion breccia. These authors were the first to identify

the volatile component and relate the explosive nature of these breccia pipes to the Hicks Dome structure.

Bradbury et al. (1955) investigated and reported on the concentration of uranium and the radioactivity within samples of clay, breccia, and fluorite from an approximately 4-mi<sup>2</sup> (10-km<sup>2</sup>) area at the apex of Hicks Dome and scattered at other locations throughout southeastern Illinois. Although the source of the radioactivity was unresolved, the authors came to two conclusions: (1) the radioactivity was not associated with the deposition of fluorite within the IKFD, and (2) the source of radioactivity could be associated with hydrothermal activity or the black shale of the New Albany Group. Two peridotite dikes sampled were moderately radioactive, as were the drill cuttings from the Hamp Well explosion breccia. The authors stated that the radioactivity within the clay is related to groundwater that probably derived the uranium from the black shale of the New Albany Group. The authors also postulated that hydrothermal solutions created some concentration of radioactive material near the crest of Hicks Dome. The radioactivity was calculated as percentage of triuranium octoxide ( $\text{U}_3\text{O}_8$ ), and values ranged from almost zero for the fluorite ore to 0.02% for clays at the crest of Hicks Dome. The black shale of the New Albany Group averaged 0.006%  $\text{U}_3\text{O}_8$ .

Clegg and Bradbury (1956) described the igneous rocks of southern Illinois and their economic significance. Although their study was primarily related to the effects these dikes and sills had on the Pennsylvanian coals, the study contains an excellent overview of their composition. A map of the areal extent of known igneous bodies in southeastern Illinois is included with the report. Optical petrographic analyses were conducted, but no geochemical analyses were presented.

Trace (1960) further investigated a location where Bradbury et al. (1955) reported elevated radioactivity. Results from trenching and shallow diamond drilling at Hicks Dome (sec. 30, T11S,

R8E) revealed a 10-ft-wide (3-m-wide) “tabular mass” striking N24° west dipping N85° southeast. The tabular body was reported by Trace to extend over 100 ft (30 m) down and over 260 ft (80 m) along the strike. Semiquantitative results indicated elevated concentrations of REE and thorium. The rare earth mineral was tentatively identified as a thorium-bearing rare earth phosphate. Preliminary X-ray diffraction studies determined that the mineral appeared to have the monazite structure, but the authors stated the atomic cell size appeared to be slightly smaller than monazite. The smaller atomic cell size of the sample was attributed to the high yttrium content, and the author suggested this mineral was relatively unfractionated or primitive. Quantitative spectrographic analysis of a hand-picked “monazite” (?) crystal reported the following REE oxide values (weight percentage): cerium, 16%; lanthanum, 11%; neodymium, 6%; samarium, 2%; gadolinium, 1.5%; praseodymium, 2.5%; dysprosium, 1.5%; yttrium, 4.2%; and thorium, 4.4%. Trace (1960) also reported that florencite (cerium-aluminum phosphate) was present associated with the monazite.

Baxter and Bradbury (1980) investigated drill cuttings at Hicks Dome from depths of 1,730 to 1,745 ft below the surface from the Henry Hamp Jr. Well #1 (Trace 1960). The authors separated small 100- $\mu\text{m}$  tabular, euhedral to subhedral crystals. These crystals were identified as bertrandite [ $\text{Be}_4(\text{Si}_2\text{O}_7)(\text{OH})_2$ ] through the use of X-ray diffraction analyses and optical measurements in oil immersions. Bertrandite was identified within the well cuttings and within a shale breccia dike along the west edge of Hicks Dome.

The igneous Type 1 and Type 2 varieties of Currier (as cited in Weller 1920) were studied by Lewis and Mitchell (1987), Sparlin and Lewis (1994), Denny et al. (2002), and Denny (2005). These ultramafic porphyritic rocks contained primary olivine (altered to serpentine), phlogopite, and pyroxene, with lesser amounts of apatite, magnetite, chromite, perovskite, sphene (titanite), garnet,



**Table 1** Microprobe quantitative analyses of perovskite from the Cottage Grove Dike, Saline County, Illinois, showing rare earth element values (Denny 2005)<sup>1</sup>

Sample	Sample ID							
	7_2	7_3	7_4	7_5	7_6	7_7	7_8	1_1cor
Nb <sub>2</sub> O <sub>5</sub>	0.34	0.29	0.32	0.51	0.46	0.40	0.28	0.50
SiO <sub>2</sub>	0.04	0.04	0.05	0.10	0.06	0.13	0.04	0.06
TiO <sub>2</sub>	55.53	55.06	55.29	54.95	55.47	55.23	55.00	55.42
Al <sub>2</sub> O <sub>3</sub>	0.22	0.24	0.23	0.19	0.21	0.23	0.22	0.20
Y <sub>2</sub> O <sub>3</sub>	0.01	0.00	0.01	0.04	0.05	0.03	0.01	0.05
La <sub>2</sub> O <sub>3</sub>	0.29	0.29	0.39	0.26	0.29	0.24	0.26	0.33
Ce <sub>2</sub> O <sub>3</sub>	0.72	0.85	1.01	0.67	0.69	0.86	0.94	0.55
MgO	0.04	0.04	0.04	0.03	0.03	0.04	0.04	0.05
CaO	39.40	38.54	38.18	38.88	38.55	39.07	38.64	38.94
MnO	0.02	0.05	0.00	0.04	0.00	0.04	0.05	0.01
FeO	1.28	1.53	1.26	1.45	1.40	1.32	1.53	1.32
SrO	0.17	0.17	0.15	0.23	0.22	0.18	0.13	0.21
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	98.06	97.10	96.93	97.35	97.43	97.77	97.14	97.64

Sample	1_2cor	1_2rim	1_3cor	1_3rim	1_4cor	1_4rim	1_5cor	1_5rim
Nb <sub>2</sub> O <sub>5</sub>	0.43	0.51	0.41	0.47	0.48	0.44	0.29	0.40
SiO <sub>2</sub>	0.05	0.06	0.24	0.09	0.08	0.08	0.06	0.08
TiO <sub>2</sub>	55.71	55.71	55.90	55.27	55.62	55.35	55.31	55.13
Al <sub>2</sub> O <sub>3</sub>	0.21	0.17	0.22	0.21	0.21	0.20	0.24	0.23
Y <sub>2</sub> O <sub>3</sub>	0.04	0.02	0.05	0.06	0.03	0.03	0.02	0.04
La <sub>2</sub> O <sub>3</sub>	0.14	0.13	0.29	0.25	0.25	0.21	0.35	0.19
Ce <sub>2</sub> O <sub>3</sub>	0.24	0.26	0.46	0.28	0.31	0.32	0.95	0.49
MgO	0.04	0.03	0.11	0.06	0.06	0.06	0.06	0.06
CaO	39.31	39.45	38.58	39.43	39.47	39.06	38.96	39.33
MnO	0.04	0.01	0.00	0.04	0.02	0.04	0.03	0.02
FeO	1.26	1.16	1.21	1.40	1.23	1.23	1.41	1.26
SrO	0.19	0.26	0.22	0.24	0.19	0.21	0.17	0.23
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	97.66	97.77	97.69	97.80	97.95	97.23	97.85	97.46

<sup>1</sup>All values are weight percentages. Analysis performed at Texas A&M University with a Cameca SX50 electron microscope.

chlorite, and carbonate. All investigations concluded these rocks were properly classified as alnöite. Alnöite is an ultrabasic lamprophyre composed primarily of biotite with or without olivine, melilite, carbonate, and commonly perovskite. Alnöite is a silica-deficient igneous rock that may grade into kimberlite with an increase in forsterite and diminution of augite, or into carbonatite with an increase of carbonate (Williams et al. 1982). Lewis and Mitchell (1987) suggested that similar igneous

intrusions along the Reelfoot Rift were part of a large alnöite province, which they called the Wauboukigou Province. Denny (2005) analyzed several minerals by using electron microscopic quantitative techniques. The rims and cores of several perovskite crystals from the Cottage Grove Dike in Saline County were characterized by electron microscopy to contain about 1% REE (Table 1). This study also identified a pelletal-lapilli texture in a few samples. The pelletal-lapilli texture was speculated to be a

result of the explosive release of volatiles into the atmosphere (Denny 2005). This explosive vent is located approximately 20 mi (32 km) north of Hicks Dome and indicates that venting of the regional ultramafic body occurred in several locations.

Bradbury and Baxter (1992) studied the Type 3 “volcanic” variety of Currier (as cited in Weller 1920) at the apex of Hicks Dome. The clast geometry and composition of the breccia bodies led Bradbury

and Baxter to three classifications: (1) vent breccias, (2) carbonatitic breccias, and (3) shatter breccias. The shatter breccias are dike-like intrusive bodies containing angular to subrounded clasts of country rock that were ripped up and shattered in places with little vertical ascent. Carbonatitic breccias are composed of both igneous and sedimentary clasts set in a matrix of igneous carbonate. Bradbury and Baxter (1992) theorized that this style of breccia was a result of explosive release of CO<sub>2</sub>-rich gas exsolving from an alkaline ultramafic magma at depth. Vent breccias are described as bodies of indeterminate form, usually silicified, that may contain sedimentary fragments originating from great depths. Although Bradbury and Baxter performed major oxide and trace element analyses of this breccia, the samples were not analyzed for REE.

Jackson and Christiansen (1993) estimated that 62,000 metric tons of rare earth oxides were present at Hicks Dome associated with the low-grade monazite mineralization previously identified by Trace (1960). Long et al. (2010) reported that REE mineralization was present in breccia associated with fluorite, calcite, pyrite, sphalerite, and galena, and they speculated these minerals are present at depths of approximately 3,000 ft (1,000 m) under the center of Hicks Dome.

## PROCEDURES FOR THIS INVESTIGATION

Samples of igneous breccia and fluorite ore were collected in 2010 and 2011 (Figure 3). These samples were examined through standard optical techniques, and several samples were selected for geochemical analyses and electron microprobe analyses. The methods of each procedure are described below.

### Geochemical Analyses

All geochemical analyses were performed at ALS Chemex (Reno, Nevada). The samples were analyzed through inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled argon plasma-

mass spectrometry (ICP-MS). The geochemical procedures from ALS Chemex for ICP-AES and ICP-MS (information supplied by ALS Chemex, exploration geochemistry) are as follows:

In plasma emission spectroscopy, a sample solution is introduced into the core of inductively coupled argon plasma (ICP) at a temperature of approximately 8000°C. At this temperature, all elements become thermally excited and emit light at their characteristic wavelengths. This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected by wavelength and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards. This measurement process is a form of atomic emission spectroscopy (AES).

In plasma mass spectroscopy, the ICP is once again used as an excitation source for the elements of interest. However, in contrast to plasma emission spectroscopy, the plasma in ICP-MS is used to generate ions that are then introduced to the mass spectrometer. These ions are separated and collected according to their mass to charge ratios. The constituents of an unknown sample can then be identified and measured. ICP-MS offers extremely high sensitivity to a wide range of elements.

### Petrographic Analyses

Thin sections were cut from several of the igneous rocks and breccia at the Illinois State Geological Survey (ISGS) Core Laboratory. The thin sections were studied with a polarizing microscope, and several digital images were collected. A few minerals could be identified through these microscopic examinations, but the source of the REE mineralization could not be verified. It was determined that electron microscopy would offer the resolution needed to determine the source of the REE.

## Microprobe Analyses

Electron microprobe analyses were conducted under the direction of Renald Guillemette at the Electron Microprobe Laboratory at Texas A&M University in College Station. The electron microprobe emits an electron beam that travels in an evacuated column through a series of magnetic lenses designed to focus the electrons to a very fine spot. As the electron beam hits a spot on the sample, secondary electrons are loosened from the surface. The energy produced results from electron transitions from outer to inner atomic orbital sites. Near the bottom of the column, a set of scanning coils moves the focused beam back and forth across the specimen. A detector counts the electrons and sends a signal to an amplifier. The backscattered electron image is built up from the number of electrons emitted from each spot on the sample, yielding an image of the section viewed on a computer monitor that can be downloaded for printing. The image is grayscale, but image processing utilizing grayscale threshold values and applying color values can create a false-color image. The electron transitions are accompanied by a release of electromagnetic radiation and fluorescent X-rays. An X-ray analyzer is capable of acquiring an energy dispersive X-ray spectrum of the sample. A quantitative analysis can be performed by comparing standards of known composition.

## RESULTS OF INVESTIGATIONS

### Geochemical Analyses (ICP-MS and ICP-AES)

Ten samples were submitted for geochemical analyses. These samples are described below, the results of geochemical analyses are given in Table 2, and sample locations are given in Figure 3. The samples were either fluorite ore or Permian igneous intrusions.

Sample PWL-1 was collected from an underground coal mine in Saline County, Illinois. This sample was obtained at the Peabody Willow Lake Coal Mine from the edge of a vertical ultramafic igneous dike that was about

**Table 2** Geochemical analyses for rare earth elements (REE), trace elements, and whole rock of igneous rocks and fluorite ore samples from southeast Illinois<sup>1</sup>

	Ultramafic igneous types and diatremes						Fluorite and ore-stage calcite			
	PWL-01	Ham-01	He-01	He-will-01	KR-3	Fsb-38	KR-1	KR-2	Cr-01	He-HD-01
<i>REE</i>										
La	84.00	88.50	74.30	70.70	293.00	290.00	3.90	30.20	1.10	1.20
Ce	157.50	173.50	123.00	128.00	467.00	535.00	11.00	79.60	1.50	2.00
Pr	17.55	19.70	13.35	13.20	45.50	61.00	1.87	10.95	0.20	0.32
Nd	64.20	75.40	44.90	45.90	143.00	228.00	9.20	48.00	1.00	1.90
Sm	10.75	13.35	7.07	7.43	17.55	37.60	2.56	11.95	0.47	0.61
Eu	3.12	3.64	2.01	2.02	4.27	9.93	1.20	5.62	0.20	0.31
Gd	9.82	8.50	6.69	4.43	17.15	22.90	2.72	11.50	1.11	0.94
Tb	1.08	1.17	0.78	0.76	1.70	3.11	0.36	1.94	0.17	0.13
Dy	4.35	5.34	3.87	4.14	6.70	15.70	2.09	11.05	0.97	0.71
Ho	0.75	0.87	0.80	0.78	1.30	2.68	0.39	2.56	0.18	0.13
Er	1.87	1.83	2.14	1.99	3.59	5.82	0.90	7.16	0.40	0.26
Tm	0.15	0.24	0.25	0.30	0.38	0.78	0.07	1.09	0.03	0.01
Yb	1.09	1.19	1.84	2.03	2.47	4.21	0.51	7.31	0.17	0.12
Lu	0.11	0.16	0.25	0.30	0.33	0.52	0.04	1.00	0.02	0.01
Y	17.30	20.80	19.10	19.80	29.90	67.90	16.00	94.20	17.50	14.80
REE total (ppm)	373.64	414.19	300.35	301.78	1,033.84	1,285.15	52.81	324.13	25.02	23.45
<i>Trace element</i>										
Ag	2.00	<1.00	10.00	<1.00	3.00	<1.00	8.00	<1.00	<1.00	<1.00
Ba	592.00	1,075.00	806.00	944.00	597.00	1,515.00	18.00	19.80	319.00	3.10
Co	58.90	73.40	4.40	3.90	15.30	40.50	1.90	1.10	0.90	0.80
Cr	860.00	770.00	30.00	20.00	30.00	160.00	20.00	10.00	10.00	<10.00
Cs	1.10	1.02	1.45	1.58	0.77	5.92	0.03	0.11	0.15	0.03
Cu	37.00	100.00	<5.00	59.00	9.00	70.00	269.00	1,170.00	<5.00	<5.00
Ga	13.20	15.20	31.70	34.90	13.50	19.00	0.50	1.40	0.50	0.20
Hf	6.20	5.70	21.20	22.70	7.00	15.90	0.40	0.60	<0.20	0.80
Mo	2.00	7.00	5.00	4.00	3.00	<2.00	<2.00	<2.00	<2.00	<2.00
Nb	118.50	133.00	603.00	573.00	155.00	231.00	3.30	2.70	2.80	1.40
Ni	384.00	401.00	14.00	12.00	16.00	60.00	17.00	9.00	<5.00	<5.00
Pb	52.00	12.00	21.00	18.00	59.00	19.00	>10,000	238.00	<5.00	<5.00
Rb	45.80	78.80	106.50	140.50	35.40	134.00	1.50	4.10	3.30	0.60
Sn	2.00	2.00	2.00	3.00	2.00	4.00	<1.00	4.00	<1.00	<1.00
Sr	482.00	470.00	848.00	765.00	1,315.00	3,040.00	161.00	203.00	98.10	32.20
Ta	6.80	7.70	21.80	22.30	5.80	14.40	0.20	<0.10	0.10	<0.10
Th	9.58	11.35	38.00	43.40	13.80	20.60	0.31	1.06	0.66	0.20
Tl	<0.50	0.90	<0.50	<0.50		<0.50	<0.50	<0.50	<0.50	<0.50

*Continued on next page*

Table 2 Continued.

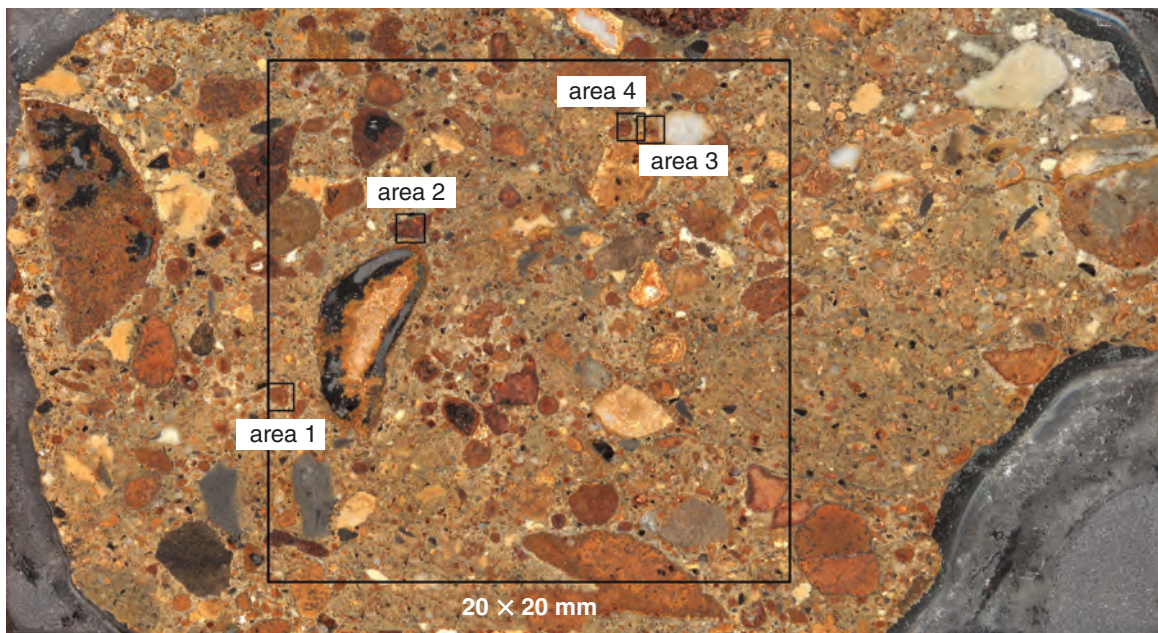
	Ultramafic igneous types and diatremes						Fluorite and ore-stage calcite			
	PWL-01	Ham-01	He-01	He-will-01	KR-3	Fsb-38	KR-1	KR-2	Cr-01	He-HD-01
U	2.46	2.94	17.95	21.30	5.55	7.95	0.07	0.24	0.47	0.07
V	315.00	280.00	57.00	55.00	135.00	237.00	10.00	9.00	8.00	<5.00
W	1.00	2.00	2.00	3.00	3.00	12.00	1.00	1.00	1.00	1.00
Zn	45.00	345.00	135.00	127.00	107.00	203.00	<5.00	<5.00	12.00	<5.00
Zr	244.00	257.00	1,340.00	1,490.00	310.00	972.00	21.00	28.00	10.00	42.00
<i>Whole rock</i>										
SiO <sub>2</sub>	17.50	32.30	53.10	53.80	36.90	24.70	6.87	12.75	3.91	0.52
Al <sub>2</sub> O <sub>3</sub>	6.16	6.45	18.35	19.00	7.32	5.40	0.09	0.53	0.52	0.15
Fe <sub>2</sub> O <sub>3</sub>	7.28	13.45	3.65	3.88	7.01	13.80	0.31	0.57	0.32	0.06
CaO	29.00	13.60	2.67	2.63	15.20	20.00	52.90	50.00	65.30	66.60
MgO	5.30	15.45	1.04	1.09	5.80	7.84	0.21	0.31	1.21	0.01
Na <sub>2</sub> O	0.28	0.22	8.58	8.08	2.13	1.48	0.02	0.02	0.07	0.04
K <sub>2</sub> O	0.98	2.07	4.11	4.70	1.42	3.79	0.01	0.14	0.08	0.03
Cr <sub>2</sub> O <sub>3</sub>	0.13	0.11	<0.01	<0.01	0.01	0.02	<0.01	<0.01	<0.01	<0.01
TiO <sub>2</sub>	3.64	3.93	0.44	0.47	1.19	3.25	0.02	0.04	0.02	<0.01
MnO	0.26	0.20	0.19	0.19	0.20	0.35	0.04	0.07	0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	0.81	0.86	0.22	0.23	0.79	2.79	0.04	0.01	0.05	0.03
SrO	0.06	0.06	0.11	0.09	0.17	0.39	0.02	0.03	0.01	<0.01
BaO	0.07	0.12	0.09	0.10	0.07	0.17	<0.01	<0.01	0.04	<0.01
LOI	27.40	9.77	6.49	4.99	21.40	14.95	32.20	36.70	4.65	0.70
Total wt%	98.90	98.60	99.00	99.30	99.60	98.90	92.70	101.00	76.10	68.10
F %	0.15	0.39	0.15	0.14	0.10	0.76	7.47	1.33	**	**

<sup>1</sup>Samples analyzed by ALS Chemex (Reno, NV). REE and trace elements analyzed by ICP-MS (values ppm); < indicates less than the detection limit. Whole rock analyzed by ICP-AES (values wt%); < indicates less than the detection limit; \*\* indicates not able to certify the results. LOI indicates loss on ignition.

10 ft (3 m) wide. This sample was a light gray fine-grained lamprophyre. The sample was highly altered, and calcite was the predominant mineral observed in the hand sample. Petrographic examinations revealed that the sample was completely altered. Outlines of prismatic laths were observed but were completely altered to calcite. Some chlorite and serpentine were also observed, and the sample was fine to very fine grained. Sample He-1 was collected from an outcrop of an igneous breccia/diatreme in Pope County, Illinois. This feature was not well exposed, but several cobbles and small boulders were present along a ravine and near the top of a small

hill. The sample selected for analyses was an ultramafic cobble found along the stream. The ultramafic rock is dark green, highly altered, and moderately weathered or oxidized. Several millimeter-sized angular clasts of fluorite enclosed in the fine-grained matrix were observed in several additional cobbles. The spatial extent and geometry of this feature are not known, but a project is being conducted as part of an M.S. thesis at Southern Illinois University to document the areal extent and geometry of this feature. Sample KR-1 was composed of low-grade fluorite ore from an abandoned underground mine. This sample contained calcite, galena, and purple

fluorite and was collected from surface tailings at the Lee Mine in Hardin County. Sample KR-2 was from an exploration pit associated with the abandoned Lacey Mine south of Hicks Dome. This sample was composed of calcite, purple fluorite, and minor green copper oxidation minerals. The sample was considered low-grade fluorite ore. Sample KR-3 was from the Sparks Hill Diatreme west of Hicks Dome. This sample was an autolith breccia or diatreme and contained several well-rounded clasts of siliceous "quartz" and unidentified autolith clasts. Some pyrite was also observed in some of the clasts. The matrix was fine-grained and could not be resolved



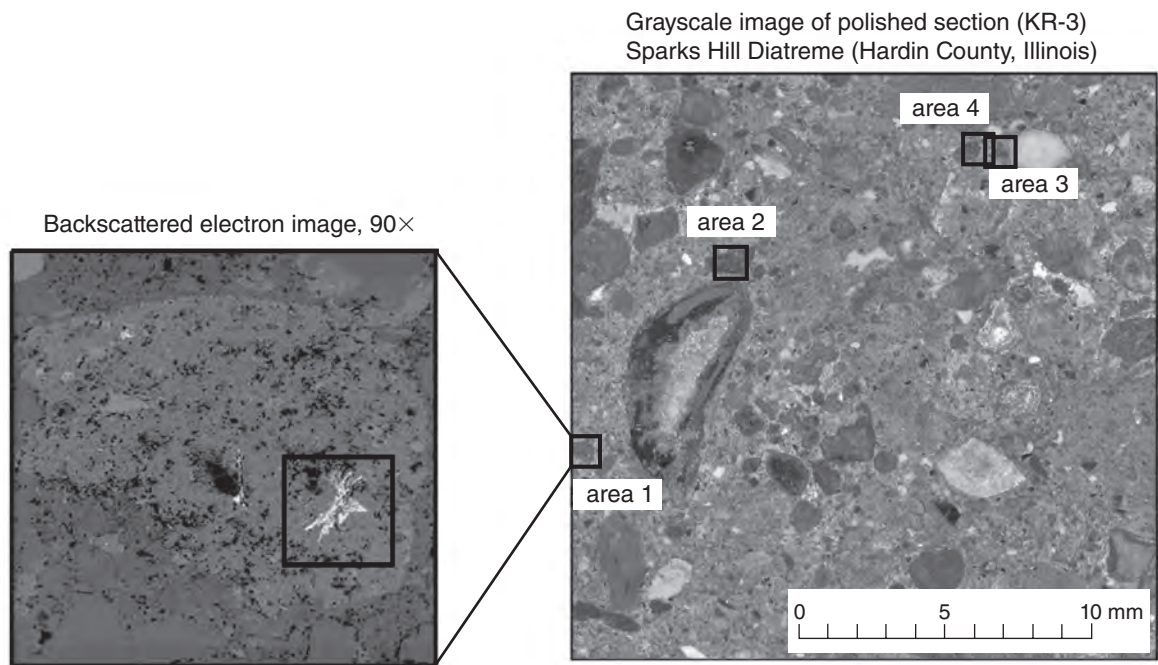
**Figure 4** Polished section of sample KR-3 showing the locations of electron microprobe investigations.

through standard petrographic techniques. Sample FSB-38 was from a drill core near the center of Hicks Dome. The sample was an ultramafic igneous rock that was recovered from over 3,000 ft (1,000 m) below the surface. Sample Ham-01 was from an Illinois Department of Transportation drill core from a bridge boring along Illinois Route 142 in Saline County, 2 mi (3.2 km) north of Eldorado, Illinois. The drillers encountered this sample beneath a few feet of soil. It is theorized this sample was from an ultramafic igneous dike. Sample He-will-01 was from the Williams diatreme, also called Hart Creek Breccia. A sample from this diatreme was collected in 2010 and labeled He-1. This diatreme was particularly interesting because of the angular chips of fluorite embedded within the lamprophyre. The second sample from this location also allowed the precision of the geochemical analyses to be compared. Sample He-HD-01 was clear or colorless fluorite found at the surface near the northwestern portion of Hicks Dome. This sample was high-grade fluorite ore, most likely acid grade. Sample CR-01 was banded fluorite ore (“coon-tail ore”) from the Hastie Quarry in Hardin County near Cave-in-Rock, Illinois. This sample was also very high grade fluorite ore.

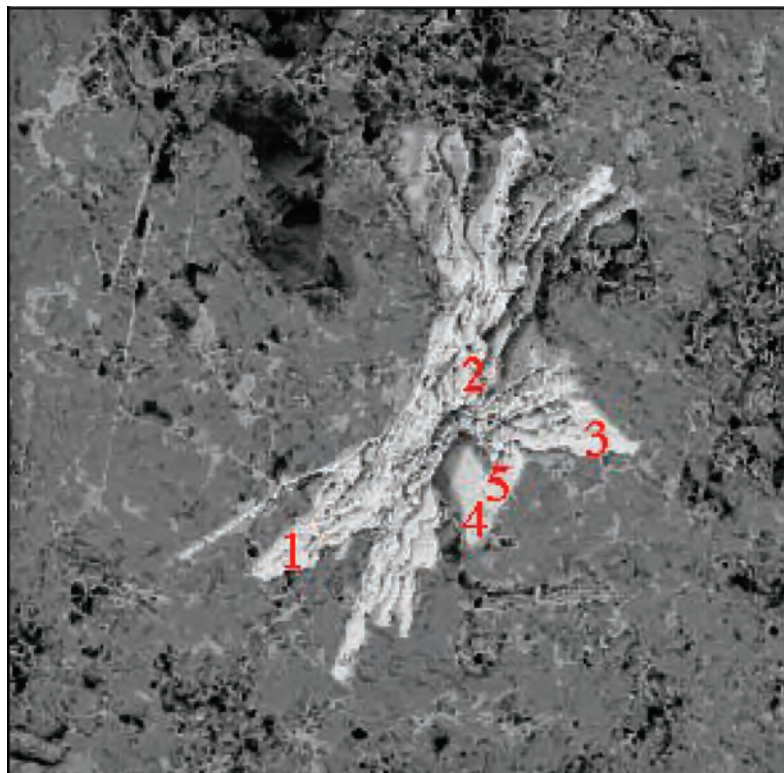
### Electron Microscopy

Sample KR-3 was selected for additional analyses because of relatively large REE values (Table 2). Sample KR-3 was from the Sparks Hill Diatreme in the Karbers Ridge Quadrangle (Figure 3). The sample was composed of rounded to subangular clasts of country rock set in a fine-grained gray to tan matrix (Figure 4). Clasts appeared to be mostly from sedimentary rocks and were white quartz and black shale, along with other altered unidentifiable clasts. These clasts ranged from 0.5 mm to more than 10 mm in diameter, and coronas and reaction rims on some of these well-rounded clasts were apparent. The sample was moderately oxidized, with brownish iron oxides on the weathered surface of the samples. A few clasts of igneous rock were observed in other samples from this outcrop, and some of the well-rounded clasts contained pyrite on fractures. Cerium and lanthanum values from the geochemical analyses were 467 and 293 ppm, respectively. Electron microprobe analysis was conducted to determine the source of these relatively high REE concentrations. The sample was first scanned with a Cameca SX50 electron microprobe at the Electron Microprobe Laboratory at Texas

A&M University to determine the mineralogy of the sample. The locations of the microprobe analyses are outlined in Figure 5, with the large square box (20 × 20 mm) defining the limits of the preliminary backscattered electron imagery. Energy-dispersive spectrometry identified four areas on this sample that contained REE, but the sizes of these grains were less than 20 μm. Area 1 contained a well-rounded clast approximately 1 mm in diameter (Figure 5). Energy-dispersive spectrometry indicated that the light-colored platy mineral within the boxed area on Figure 5 contained lanthanum. This area was magnified, and quantitative analyses were obtained from five locations (Figure 6). The results of these analyses from areas 1, 2, 3, and 4 are given in Table 3. The results indicated the source of the REE detected in the whole-rock analysis was a rare earth fluorocarbonate that was scattered throughout the rock. This fluorocarbonate contained more cerium than calcium and had a greater than 2:1 ratio of rare earth carbonate to calcium carbonate. This mineral was identified as synchysite [Ca(Ce,La,Nd,Y)(CO<sub>3</sub>)<sub>2</sub>F] through electron microprobe quantitative analyses and stoichiometric calculations. Synchysite is similar to



**Figure 5** Box at the right side is a grayscale image of sample KR-3 from Figure 4. Rectangles outline locations of electron microprobe analyses. The box at the left side of the figure is a backscattered electron image of area 1. The rectangle on the backscattered electron image shows the location of synchysite and the location of Figure 6.



**Figure 6** Enlargement of area 1 on Figure 5 showing platy synchysite and locations of microprobe analyses of A1b points (01–05) in Table 3.

**Table 3** Microprobe analyses of selected points of suspected synchysite grains<sup>1</sup>

Analysis	Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	La <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Nd <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Pr <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	CaCO <sub>3</sub>	Sr	Fe	F	[–] F–CO <sub>3</sub>	Total (wt%)
A1b_pt01	34.22	14.66	13.82	4.68	2.28	29.84	0.00	1.57	3.65	11.54	93.18
A1b_pt02	35.69	17.63	12.27	4.80	1.66	32.15	0.06	1.03	4.72	14.90	95.10
A1b_pt03	38.07	18.46	14.01	5.22	2.11	32.61	0.17	1.35	3.11	9.81	105.28
A1b_pt04	36.68	17.25	13.66	4.65	2.04	31.04	0.20	1.47	1.14	3.60	104.52
A1b_pt05	37.58	19.01	12.40	5.54	0.81	31.20	0.23	0.35	1.26	3.99	104.38
A1a_pt06	37.62	19.93	11.70	5.60	1.32	32.21	0.10	0.75	3.53	11.14	101.62
A2a_pt07	37.44	23.08	9.03	5.17	0.13	31.23	0.86	1.39	3.61	11.41	100.53
A2a_pt08	35.39	20.55	9.14	5.00	0.24	31.06	0.89	2.04	3.40	10.74	96.97
A3a_pt09	36.54	20.96	10.73	4.75	1.32	30.74	0.11	0.79	4.23	13.34	96.82
A3a_pt10	33.87	19.50	10.43	4.44	1.23	32.59	0.19	0.65	3.99	12.60	94.29
A4_pt11	36.09	19.92	10.09	5.32	0.91	30.47	0.24	0.47	4.12	13.00	94.62
A4_pt12	36.92	18.13	10.93	4.49	1.54	30.99	0.08	0.87	4.32	13.65	94.62

<sup>1</sup>See Figures 5 and 6. A1 represents area 1 on Figure 5, and A2, A3, and A4 represent areas 2, 3, and 4, respectively. Values are weight percent, and a fluorine correction for cerium interference has been calculated.

other rare earth fluorocarbonates, such as parisite [Ca(Ce,La,Nd)(CO<sub>3</sub>)<sub>2</sub>F], bastnasite [(Ce,La,Y)CO<sub>3</sub>F], and rontgenite [Ca(Ce,La)(CO<sub>3</sub>)<sub>2</sub>F]. These minerals are commonly intergrown, making speciation difficult.

## CONCLUSIONS

Geochemical analyses determined that the highest REE values of the 10 samples for this investigation were from igneous rock samples, although HREE appeared to be slightly elevated in one fluorite ore sample (KR-2; Figure 7). This sample was taken from an exploration pit southwest of Hicks Dome near the Lacey Mine and was composed of crystalline calcite, purple fluorite, and minor amounts of an unidentified green copper oxidation product (Table 2, Figure 3).

Electron microprobe analyses determined that the source of the REE in sample KR-3 was a rare earth fluorocarbonate, synchysite. The identification of this mineral implies that conditions were correct within this alkaline igneous complex to concentrate the REE within the ultramafic melt. Whether these minerals are concentrated within this complex in sufficient quantities to be considered an economic resource has yet to be determined.

During crystallization of the ultramafic magma, LREE were incorporated into several minerals, such as apatite and perovskite (Table 1), which could accommodate the large cationic radius of the REE. As the crystallization of the ultramafic melt progressed, residual HREE were concentrated in the melt that may have mixed with basinal brine fluids (or MVT fluids, or both) migrating through the region. The REE that did not crystallize with early-formed igneous minerals might also have been complexed with the fluorine gases that exsolved from the residual magma (Plumlee et al. 1995). The timing of the formation of the rare earth fluorocarbonate cannot be accurately estimated, but we assume it began soon after the venting of the regional igneous system, which would have created temperature and pressure variances across the melt. The interaction of igneous melt with groundwater may have been an impetus for the explosive activity near the apex of Hicks Dome (Brown et al. 1954). Hydraulic mixing would explain the explosive nature of the diatremes, the dilation of the host rock, and the brecciated low-grade fluorite deposits at 3,000 ft (1,000 m) under Hicks Dome. The identification of the pelletal-lapilli texture (which is

indicative of venting of the igneous body to the atmosphere) within these igneous rocks 20 mi (32 km) north of Hicks Dome implies that Hicks Dome was not the only location where the igneous complex explosively vented volatiles to the surface. If this is true, and the synchysite mineralization occurred in conjunction with venting, the extent of REE mineralization may not lie solely beneath Hicks Dome.

The synchysite in the breccia may well be related to a long-suspected deep-seated carbonatite phase of this regional igneous complex. Fluorite ores are related to carbonatite intrusions at Okorusu (Namibia) and Amba Dongar (India), where they were deposited from late-stage low-temperature (130 to 160°C) hydrothermal fluids, and where the fluorine was derived from the carbonatite (Richard Hagni, Missouri University of Science and Technology, personal communication, 2011). Whether the source of fluorine for the Illinois-Kentucky fluorspar deposits was mobilized as a gaseous phase (Plumlee et al. 1995) or by aqueous MVT fluids from the deep-seated carbonatite is a subject for further investigation.





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