Geochemistry of apatite from the carbonatite and associated alkaline rocks of the Magnet Cove Igneous Complex, Hot Spring County, Arkansas

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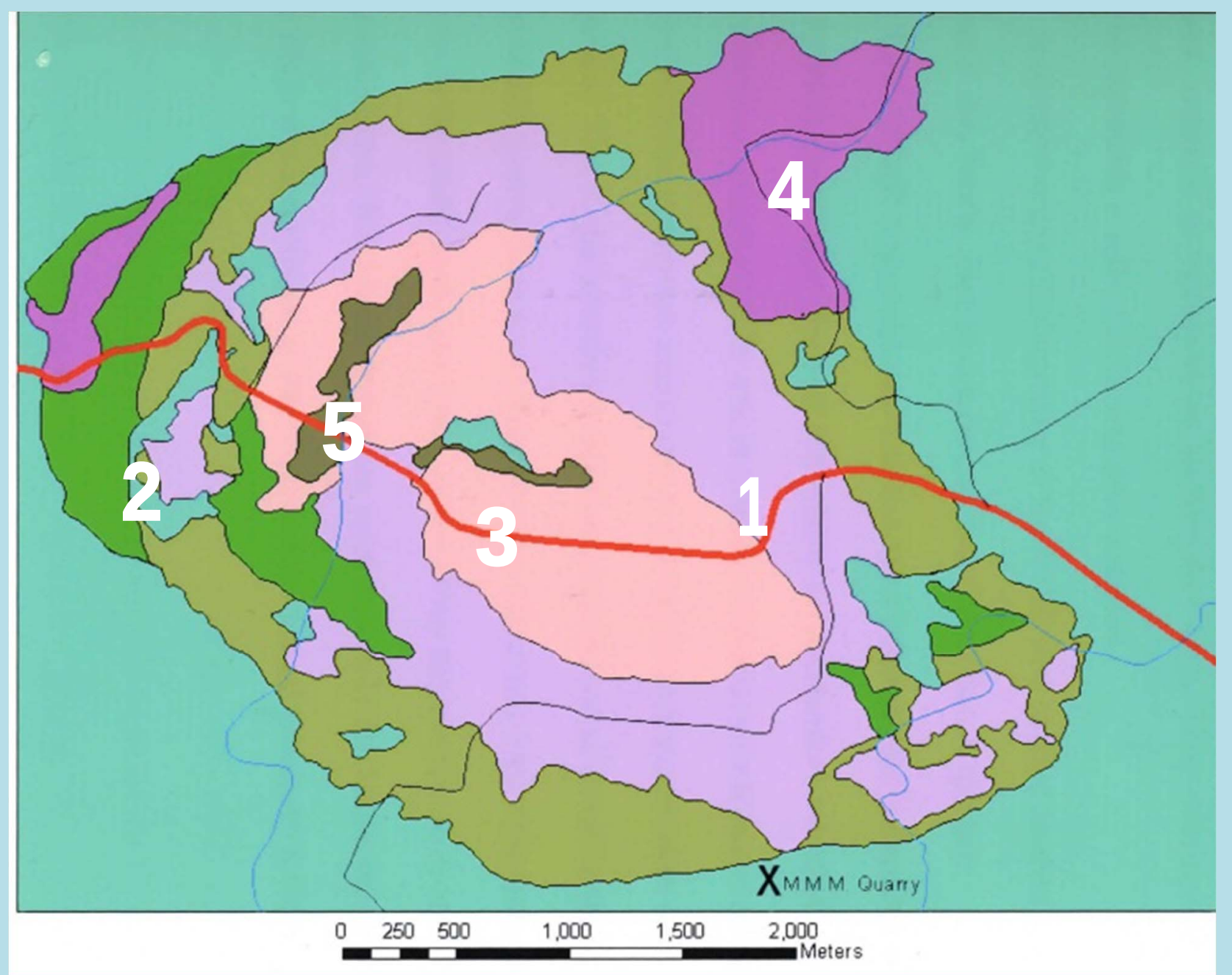
1. ABSRACT

Apatite from carbonatite and alkaline rocks from the Magnet Cove Igneous Complex in Arkansas was analyzed for major and trace element composition. Halogen concentrations were used, along with both calculated and assumed temperatures and pressures, to determine changes in HF and HCl fugacities over the time of crystallization of the magma. Additionally, apatite was analyzed for REE concentrations. These data were used to estimate the degree of differentiation between rock types that occurred over the crystallization history of the complex. Concentrations of major and minor elements (including halogens) in apatite were determined by electron probe microanalysis, and trace element concentrations were measured using laser ablation inductively coupled plasma mass spectrometry.

2. THE MAGNET COVE IGNEOUS COMPLEX



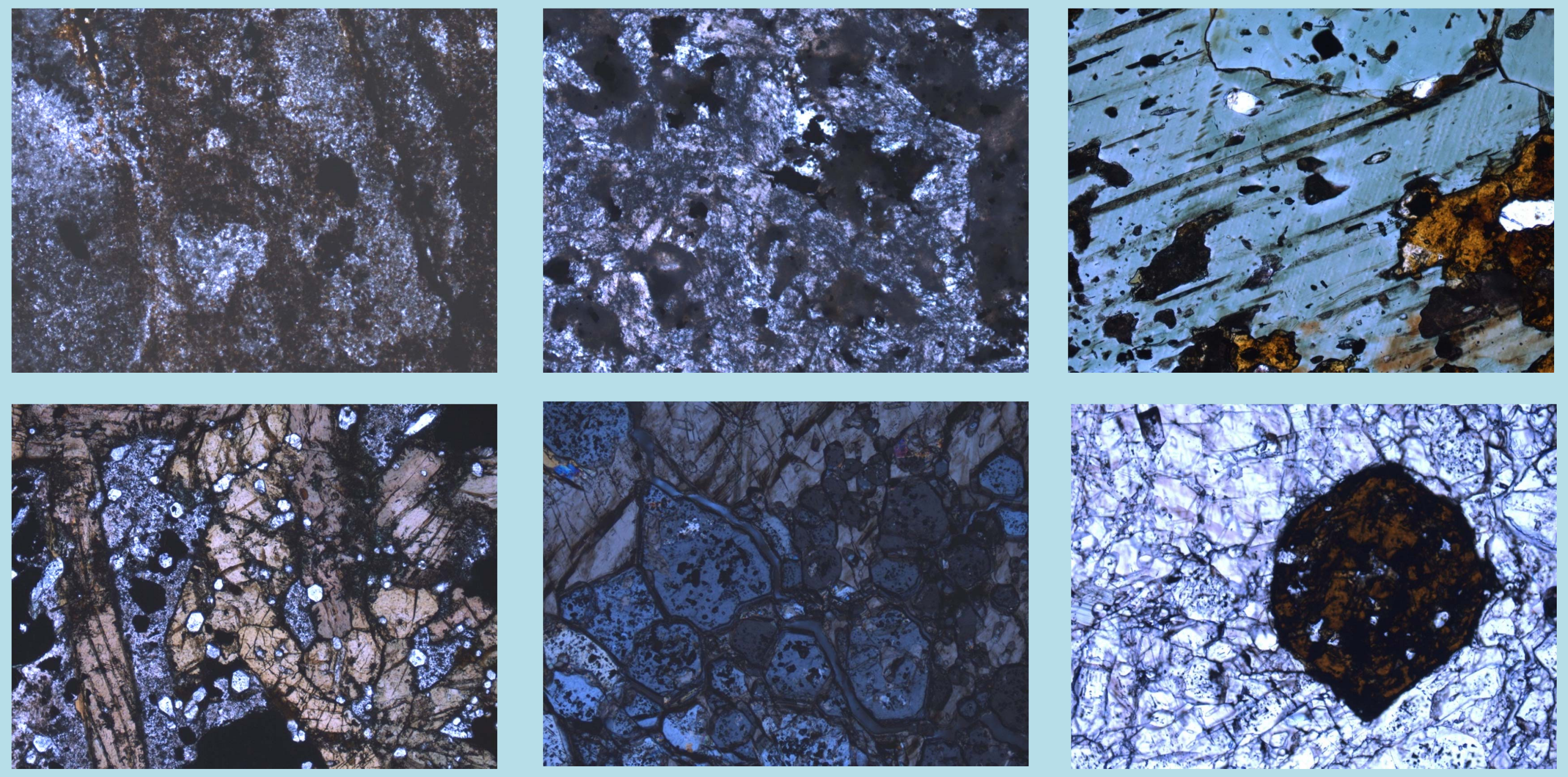
MCIC-1=Trachyte-phonolite (phonolite)
MCIC-2=Garnet pseudoleucite nepheline syenite (syenite)
MCIC-3=Biotite ijolite (ijolite)
MCIC-4=Jacupirangite
MCIC-5=Carbonatite

The Magnet Cove Igneous Complex is a carbonatite complex in the Arkansas Alkaline Belt. Carbonatites are uncommon (~330 known occurrences) igneous rocks composed of >50% carbonate minerals. They are typically associated with silica-undersaturated igneous rocks, and generally form small intrusions where a carbonatite core is surrounded by ring-shaped silicate intrusions (Wooley and Kempe, 1989). Apatite is common in the rocks of the Magnet Cove Igneous Complex. It ranges in modal abundance throughout the rock types, and can make up anywhere between 1-24% of the rock. Because of its ubiquity, composition, and resistance to subsolidus change, apatite was used as a proxy for multiple elemental systems that may have evolved and changed as the magma that formed the Magnet Cove Igneous Complex cooled.

Carbonatites are characteristically enriched in trace elements and halogens. Assuming that the Magnet Cove rocks are representative of a magma that evolved into a carbonatitic composition, with various rock types representing periods in its cooling history (Erickson and Blade, 1963), there will be systematic changes in both halogens and REE in the apatite from all of the Magnet Cove rock types.

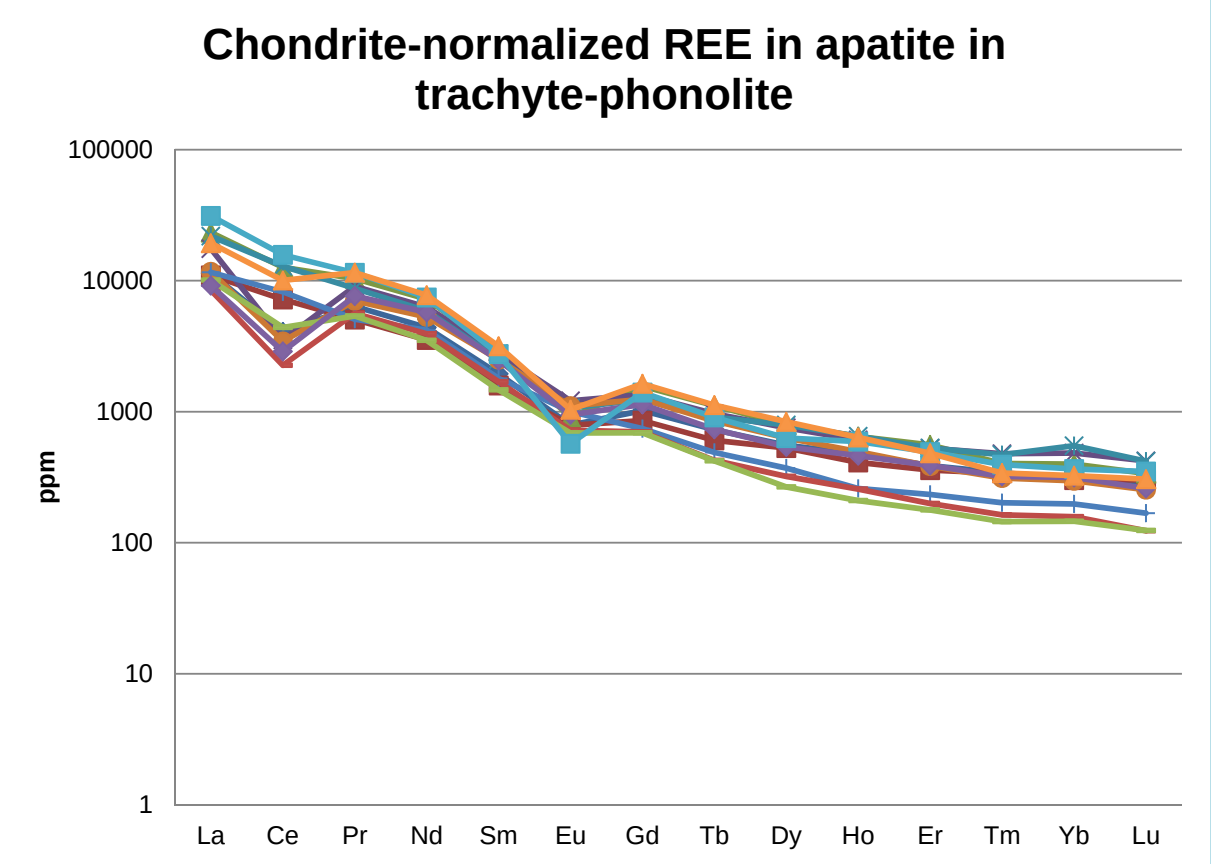
3. METHODS

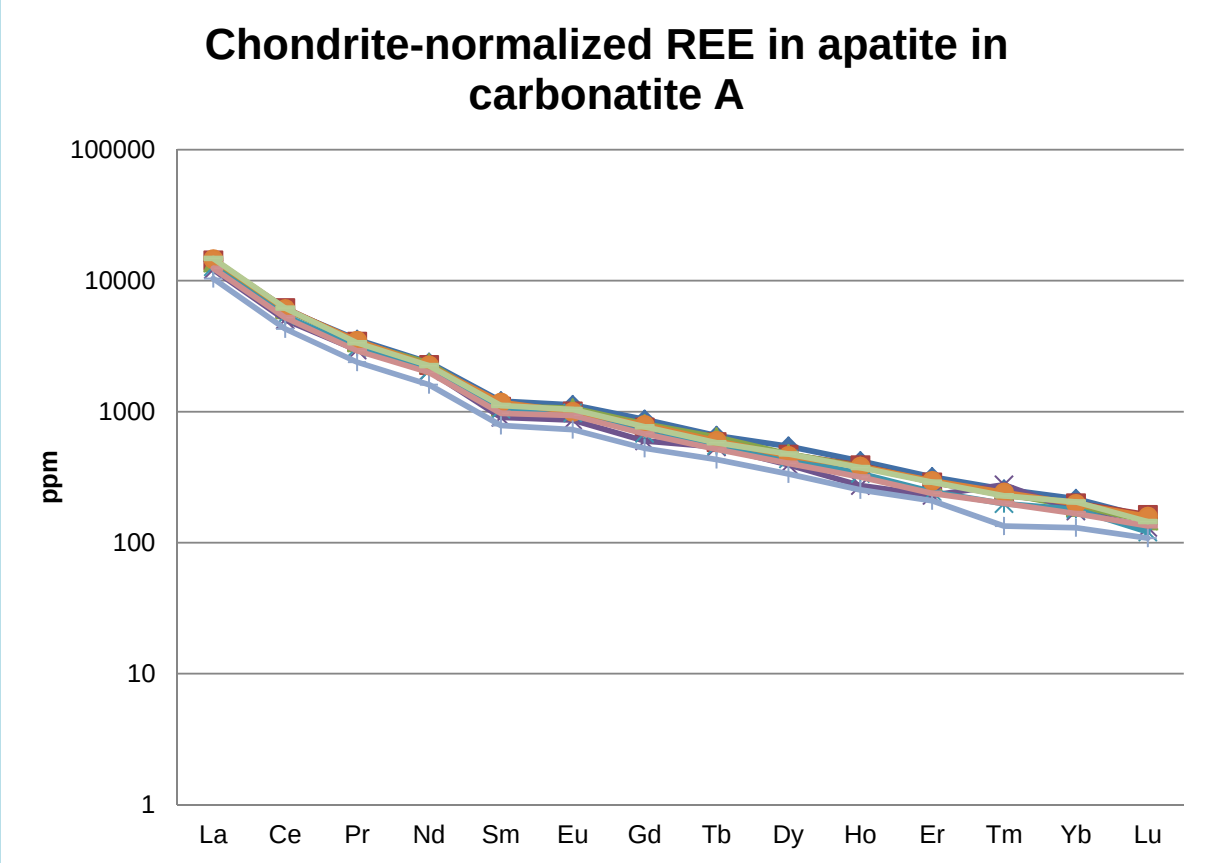
Six thin sections made from silicate and carbonate rock from the Magnet Cove Igneous Complex were made. They were examined by petrographic microscope to locate apatite for analysis. Crystals were analyzed by laser ablation inductively coupled plasma mass spectrometry for trace element concentrations, and electron probe microanalysis for major elements. Data from LA-ICP-MS measurements was reduced using the LAMTRACE program, and EPMA data on fluorine and chlorine concentrations was input into models to determine halogen fugacity ratios from each representative rock type.

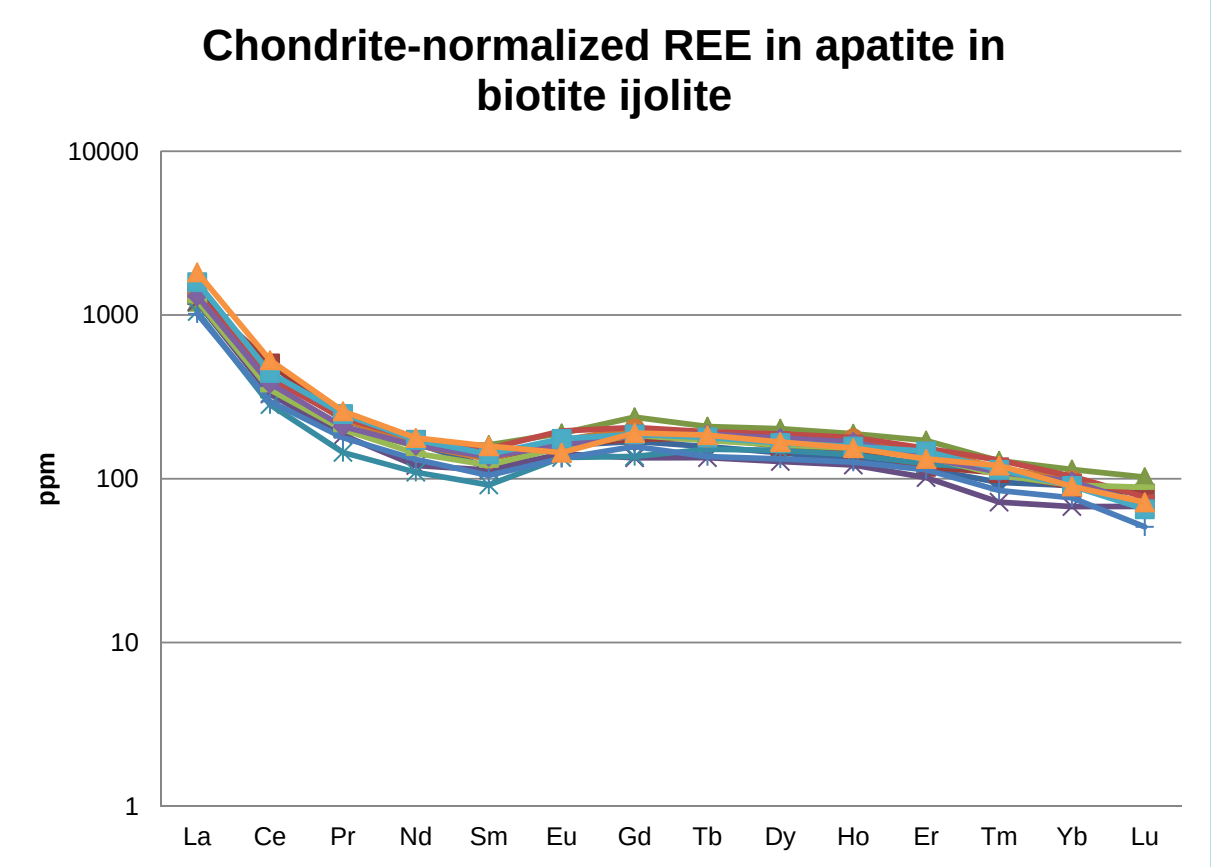


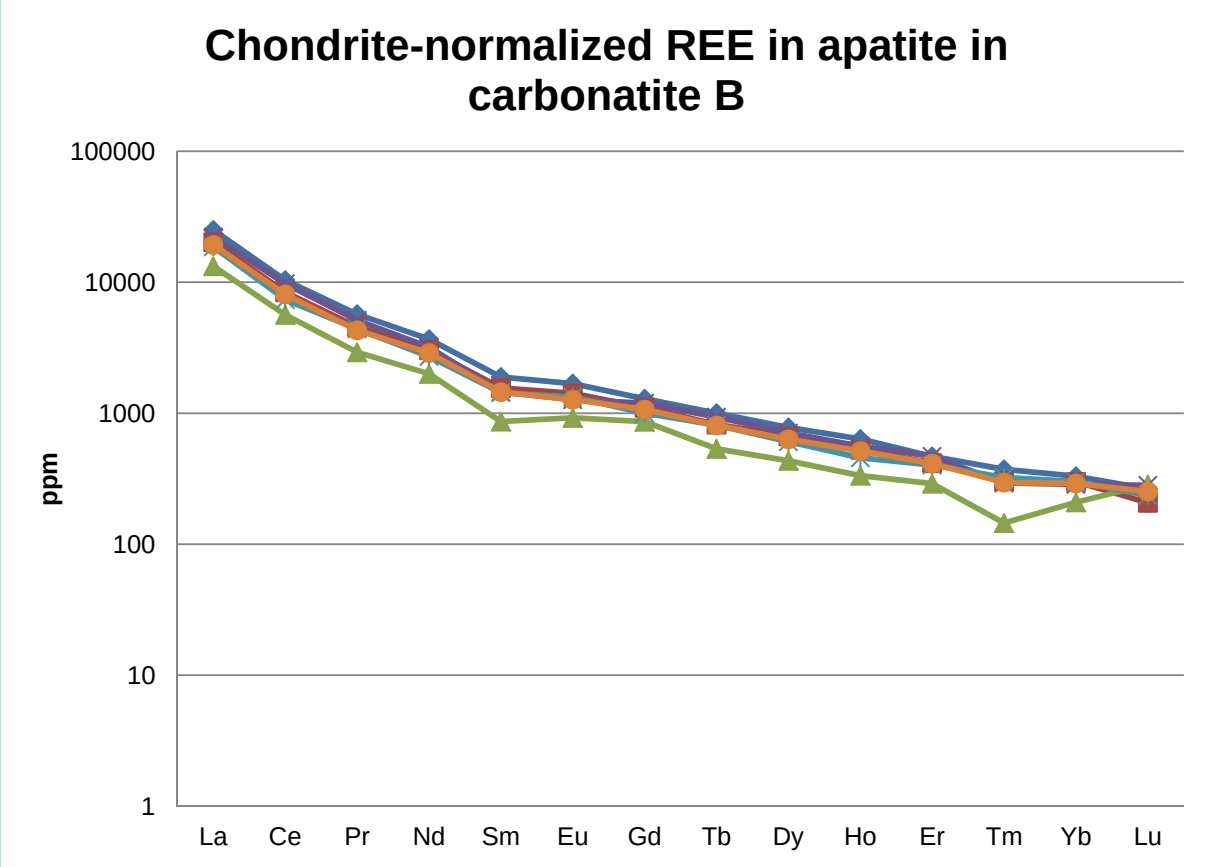
Photomicrographs showing various populations of apatite in Magnet Cove Igneous Complex rocks. Upper left: altered equant apatite in phonolite. Lower left: multiple populations of apatite within pyroxene, nepheline, and magnetite in jacupirangite. Upper middle: apatite within altered nepheline in syenite. Lower middle: cluster of equant apatite in carbonatite. Upper right: apatite within pyroxene and mica in ijolite. Lower right: zimzeyite containing apatite inclusions surrounded by equant and elongate apatite in carbonatite.

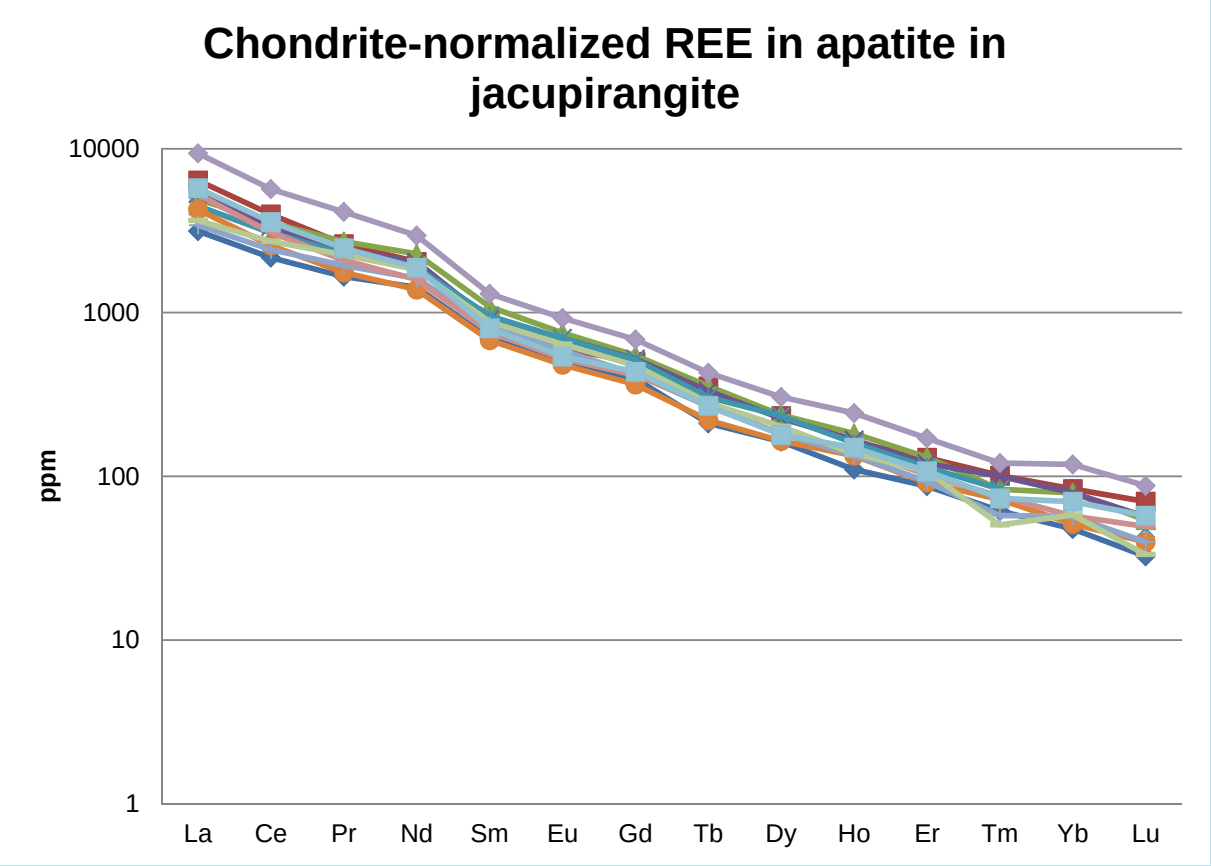
4. RARE EARTH ELEMENT GEOCHEMISTRY


Chondrite-normalized REE in apatite in trachyte-phonolite


Chondrite-normalized REE in apatite in carbonatite A


Chondrite-normalized REE in apatite in biotite ijolite

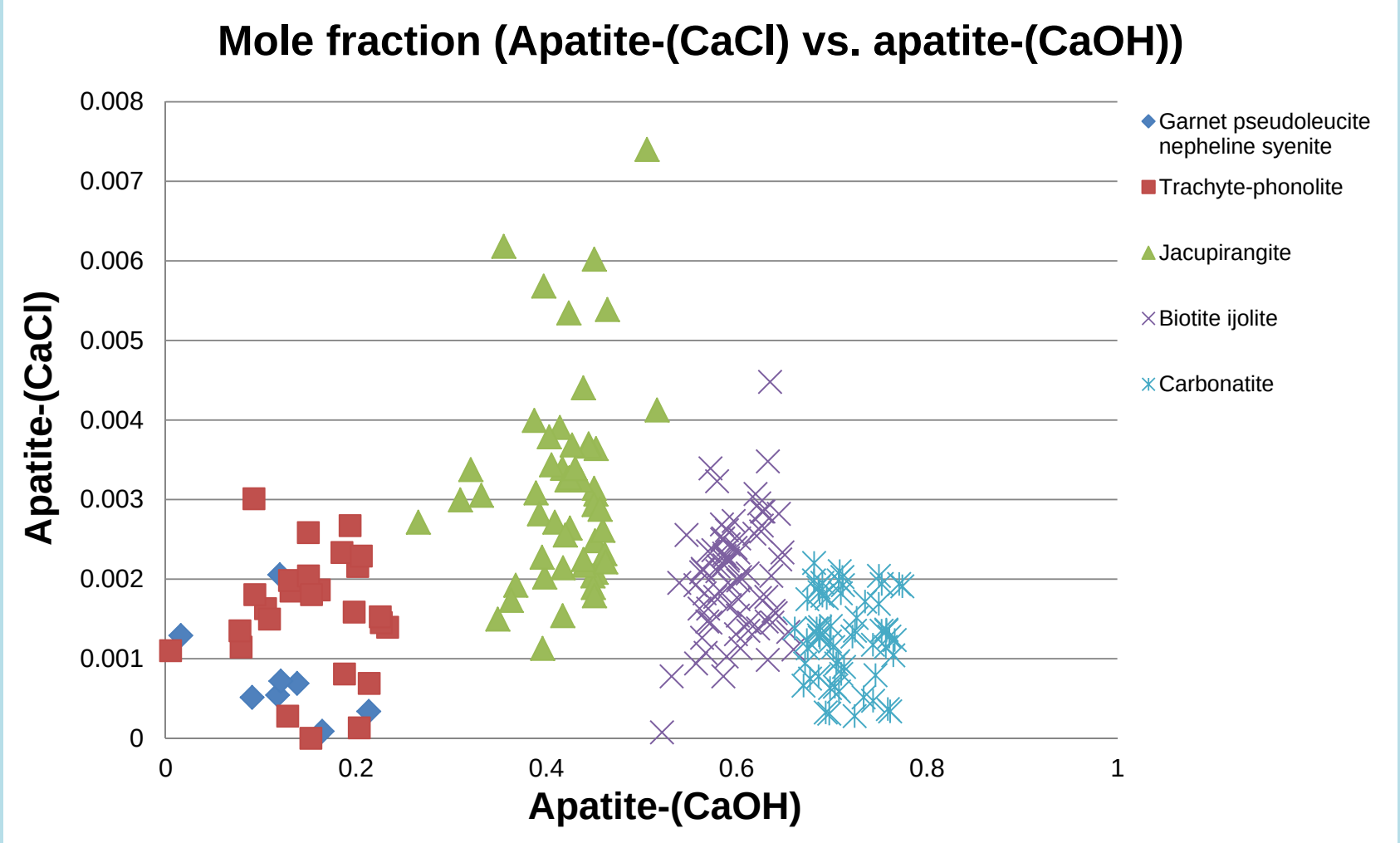

Chondrite-normalized REE in apatite in carbonatite B

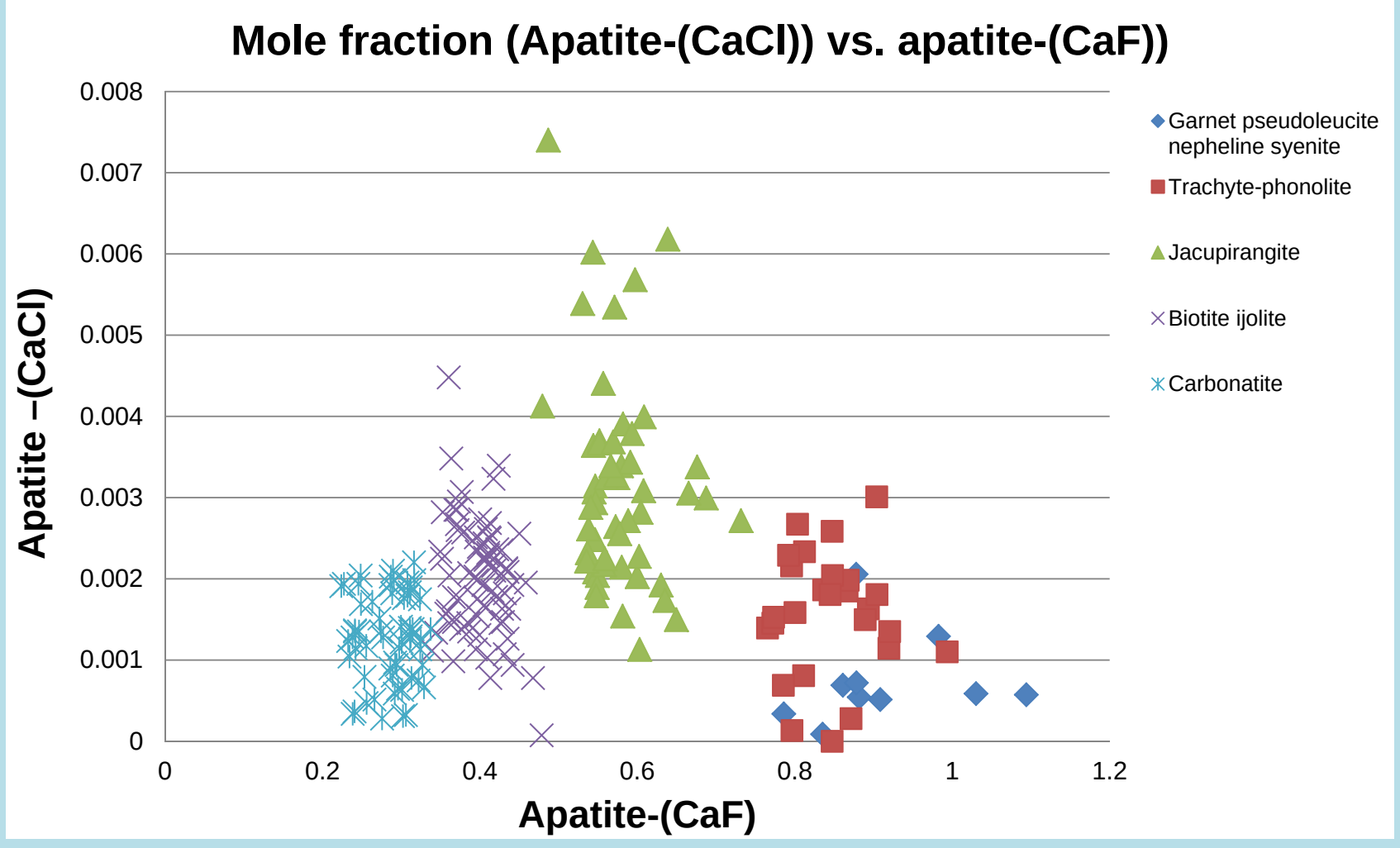

Chondrite-normalized REE in apatite in jacupirangite

Total rare earth element concentrations in apatite from the Magnet Cove Igneous Complex ranged from ~500 ppm to almost 6 weight percent. REE concentrations in apatite were strongly controlled by the presence of other REE-bearing phases in the rocks. These included titanite, perovskite, and kimzeyite, a Ti-Zr garnet. REE fractionation varied between rocks, and LREE:HREE values tended to increase with increased overall REE content in apatite. All apatite was enriched in LREE relative to HREE.

5. WHY ARE HALOGENS IMPORTANT?

Halogens, like water, can control properties of a melt. The presence of chlorine and fluorine can lower the solidus temperature of a melt significantly. The presence of halogens in a melt, along with their concentrations, can be determined in part by the presence and composition of minerals that crystallized from the melt. Apatite takes in halogens into its crystal structure in a way that allows its composition to be used as a proxy for halogen concentrations in the melt from which the apatite crystallized. Halogen concentrations in apatite from the Magnet Cove Igneous Complex were used to determine the changes in the halogen budget of the original melt that evolved and cooled to form the rocks of the Magnet Cove Igneous Complex.


Mole fraction (Apatite-(CaCl) vs. apatite-(CaOH))


Mole fraction (Apatite-(CaCl)) vs. apatite-(CaF))

6. FUGACITY

Fugacity ratios are used to express the changing concentrations of halogens and water in the melt that formed the Magnet Cove Igneous Complex rocks at different points in its crystallization history. Fugacity values are used to express overall concentrations of volatiles in a melt when it exists at varying temperatures and pressures as it evolves. Ratios of these values show how fluorine and chlorine changed in proportion to each other and to water in the melt as it cooled and evolved.

	f_{HCl}/f_{H2O}	f_{HF}/f_{H2O}
MCIC-2 (Syenite)	**2.6E-05**	**1.6E-05**
MCIC-1 (Phonolite)	**3.3E-05**	**1.6E-05**
MCIC-4 (Jacupirangite)	**1.4E-05**	**1.6E-06**
MCIC-3 (Ijolite)	**5.7E-06**	**8.1E-07**
MCIC-5A (Carbonatite)	**2.9E-06**	**5.0E-07**
MCIC-5B (Carbonatite)	**3.2E-06**	**4.5E-07**

$$\frac{f_{HCl}}{f_{H_2O}} = \frac{XAp_{(CaCl)}}{XAp_{(CaOH)}} \times \frac{1}{10\hat{}(0.04661+\left(\frac{2535.8}{T}\right)-\left(\frac{0.0303(P-1)}{T}\right)}$$

$$\frac{f_{HF}}{f_{H_2O}} = \frac{XAp_{(CaF)}}{XAp_{(CaOH)}} \times \frac{1}{10\hat{}(0.18219+\left(\frac{5301.1}{T}\right)-\left(\frac{0.0036(P-1)}{T}\right)}$$

7. CONCLUSIONS

Modeled fugacity ratios determined from halogen concentrations in apatite indicated a systematic decrease in both HF and HCl fugacity as the rocks decreased in age, while REE concentrations indicated that trace element partitioning was strongly controlled by phases in the individual rock types in the Magnet Cove Igneous Complex. These results suggest that geochemical evolution in the complex was influenced by continuous (fractional crystallization) and/or episodic (multiple episodes of magmatism from the same parental magma) processes.

8. SOURCES

Ausburn, K.R., 2006, *Geology, mineralogy, and petrology of the contact zone, southern Magnet Cove Igneous Complex, Hot Spring County, Arkansas*, M.S. thesis, Stephen F. Austin State University
Erickson, R.L., Blade, L.V., 1963, *Geochemistry and Petrology of the Alkalic Igneous Complex at Magnet Cove, Arkansas*, United States Geological Survey Professional Paper 425
Wooley, A.R., Kempe, D.R.C., 1989, *Carbonatites: Nomenclature, average chemical compositions, and element distribution*, Carbonatites, ch. 1, p. 1-14