



Rare Earth Elements in Phosphate Sample by INAA

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The present talk contains

- ❑ What is the rare earth elements
- ❑ Techniques for Measuring Rare Earth Elements
- ❑ What is neutron activation analysis
- ❑ Samples Location and Preparation
- ❑ Nuclear properties of the rare-earth nuclides
- ❑ Irradiation cycles
- ❑ Results
- ❑ Conclusion

What is the rare earth elements

The rare earth elements (REE.s) are a group of chemical elements composed of scandium, yttrium, and 15 lanthanides from La through Lu.

Periodic table of the elements

group	1*	2											13	14	15	16	17	18
	Ia**	IIa											IIIa	IVa	Va	VIa	VIIa	0
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	IIIb	IVb	Vb	VIb	VIIb	VIIIb		Ib	IIb	Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	(Uub)	(Uut)	(Uuq)	(Uup)	(Uuh)		
lanthanide series			6	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
actinide series			7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Legend:

- alkali metals
- alkaline earth metals
- halogens
- noble gases
- transition metals
- other metals
- rare earth elements (21, 39, 57–71)
lanthanide elements (57–71 only)
- actinide elements
- other nonmetals

* Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

** Numbering system widely used, especially in the U.S., from the mid-20th century.

*** Discoveries of elements 112–116 are claimed but not confirmed. Element names and symbols in parentheses are temporarily assigned by IUPAC.

Occurrence and abundance

- ❑ The rare-earth elements are not rare in nature. They are found in low concentrations throughout the Earth's crust and in high concentrations in a number of minerals.
- ❑ In the Earth's crust, the estimated (Σ REEs) ranged from 150 to 220 ppm.
- ❑ Cerium is reported to be more abundant in the Earth's crust than tin, and yttrium and neodymium more abundant than lead.
- ❑ The rare-earth elements are found as mixtures in almost all massive rock formations, in concentrations from ten to a few hundred ppm.
- ❑ The basic (or alkaline) rocks contain smaller amounts of rare earths than the acid rocks

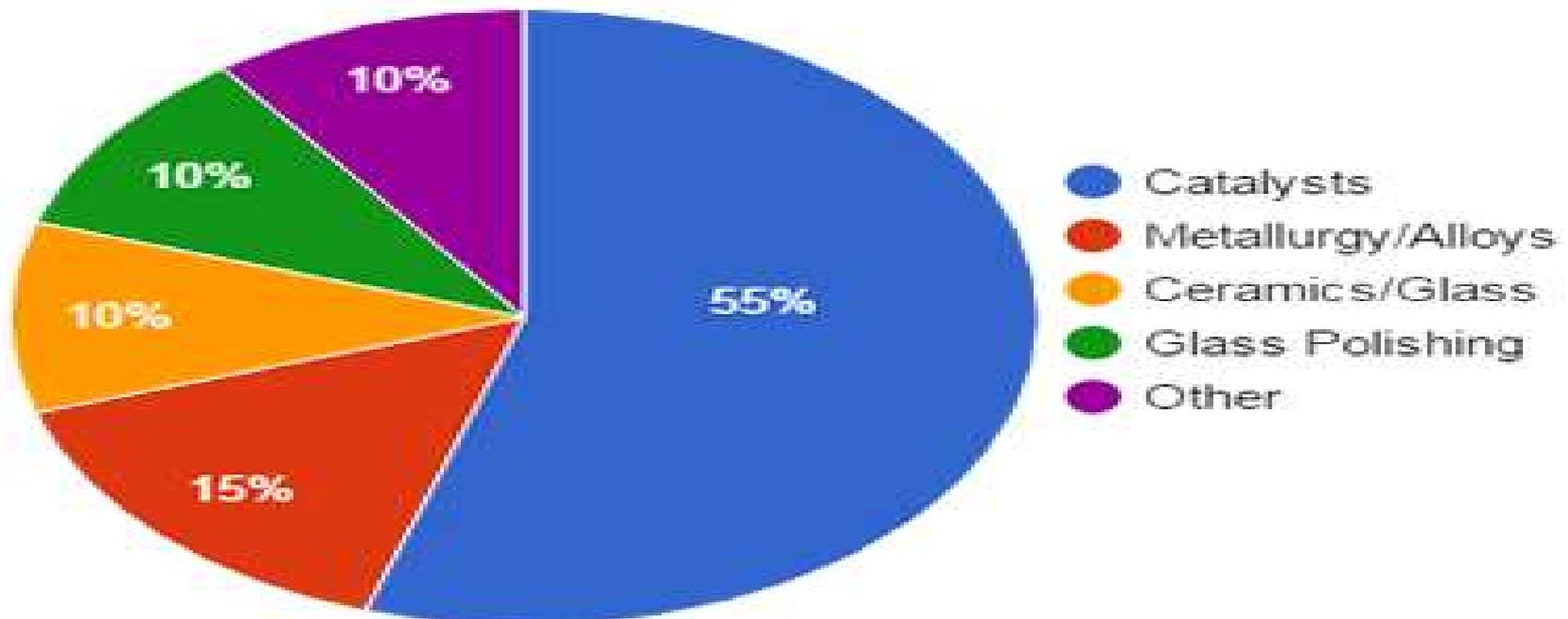
Abundance of the Naturally Occurring Rare Earth Elements

Element	Earth crust	North American Shales	West American granites
Sc	5	---	---
Y	28	35.00	31.00
La	18	39.00	49.00
Ce	60	76.00	97.00
Pr	5.5	10.30	11.00
Nd	24	37.00	42.00
Sm	6.5	7.00	7.20
Eu	1.1	2.00	1.25
Gd	6.4	6.10	5.80
Tb	0.9	1.30	0.94
Dy	4.5	---	---
Ho	1.2	1.40	1.22
Er	2.5	4.00	3.20
Tm	0.2	0.58	0.53
Yb	2.7	3.40	3.50
Lu	0.8	0.60	0.52

Application of Rare Earth Elements

REEs are becoming more and more technologically significant due to their widespread utility as fine chemicals in modern industry

Uses of Rare Earth Elements



Uses in the United States as reported by the United States Geological Survey Mineral Commodity Summary, 2017

Techniques for Measuring Rare Earth Elements

- ❑ The concentrations of REEs are usually determined by inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP -AES).
- ❑ These techniques require the sample to undergo dissolution or fusion before measurement.
- ❑ It is difficult-to-dissolve sample e.g. soil and rock.
- ❑ Neutron activation analysis (NAA) appears to be an attractive technique for determining REEs present in environmental samples; soil, sediments, plants.



Comparison between analytical methods for rare earth elements

Method	Accuracy	Sensitivity (S)	Sensitivity (L)	Multi-elemental	Sample size	Sample type
INAA	+	0	0	+	mg-kg	S,L
RNAA	+	+	+	0	mg-g	S,L
XRF	+	-		+	mg	S
AAS	-	0	+		mg-g	L
ICP-AES	0	0	+	+	mg	L
ICP-MS	0	0	+	+	mg-g	L

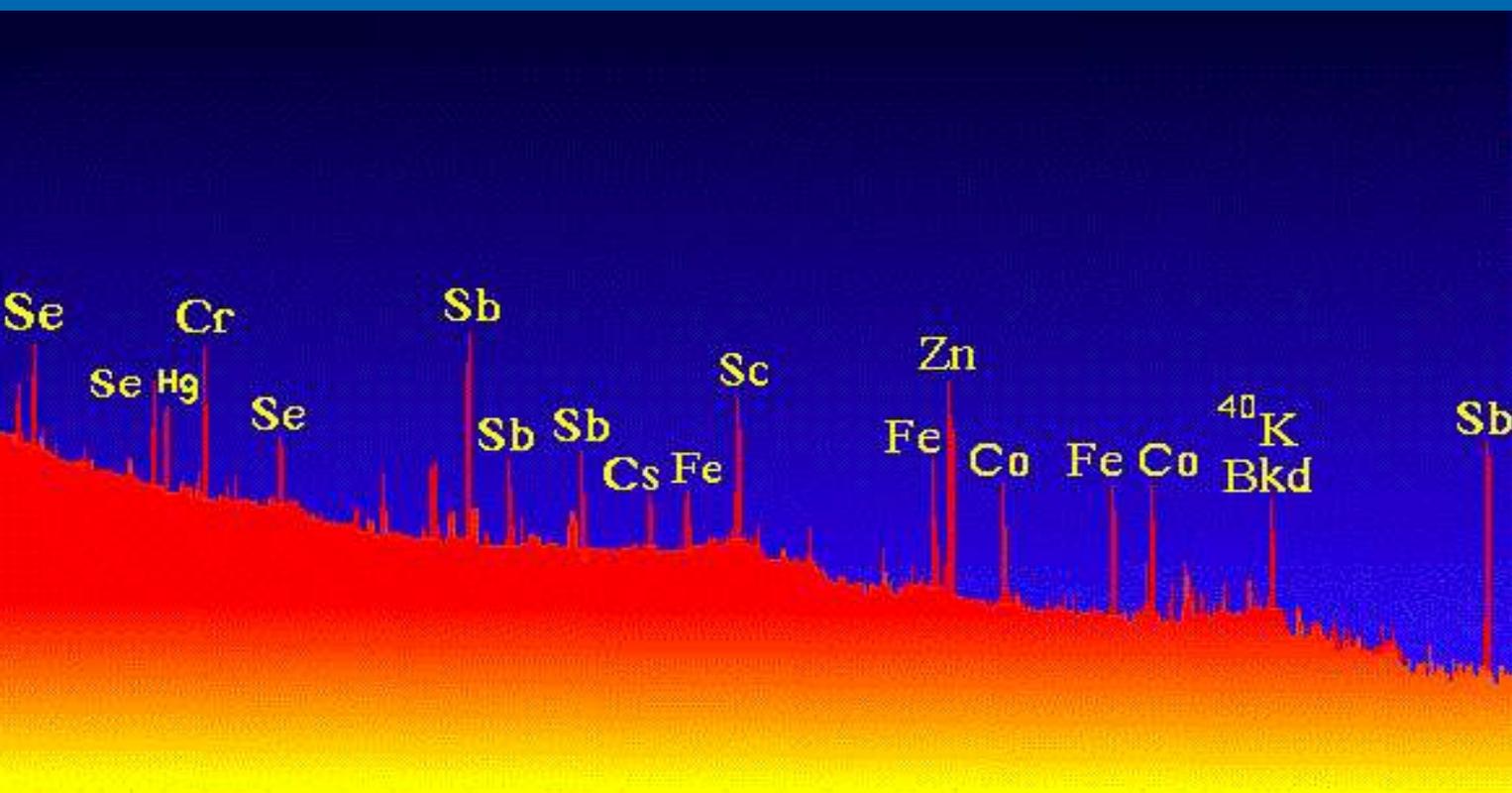
L = Aqueous solution S = Solid
+ = Good 0 = Average - = Not so good

Detection limits of REE in Nanograms by various techniques

Elements	XRF	AAS	INAA	Mass spectroscopy
La	----	20	0.1	0.1
Ce	----	200	10	0.1
Nd	60	10	10	0.4
Sm	60	10	0.05	0.5
Eu	30	1	0.0005	0.2
Yb	5000	2	0.1	0.5
Lu	----	6	0.005	0.1

What is neutron activation analysis ?

Neutron Activation Analysis (NAA) is a non-destructive technique capable of measuring up to 64 elements, many at levels of 1 $\mu\text{g}/\text{kg}$ or lower. The sample is placed in a flux of neutrons and after cooling time are measured by gamma spectroscopy.



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Weta. Bob Aronow

Applications of the NAA Technique

Neutron activation analysis techniques are widely used in the scientific, engineering, environmental and industrial disciplines such as :

- ❑ Geological Science
- ❑ Semiconductor Materials
- ❑ Soil Science
- ❑ Environmental Restoration
- ❑ Epidemiology
- ❑ Forensic Investigation
- ❑ Archaeology
- ❑ Air Filter Analysis
- ❑ Biochemistry

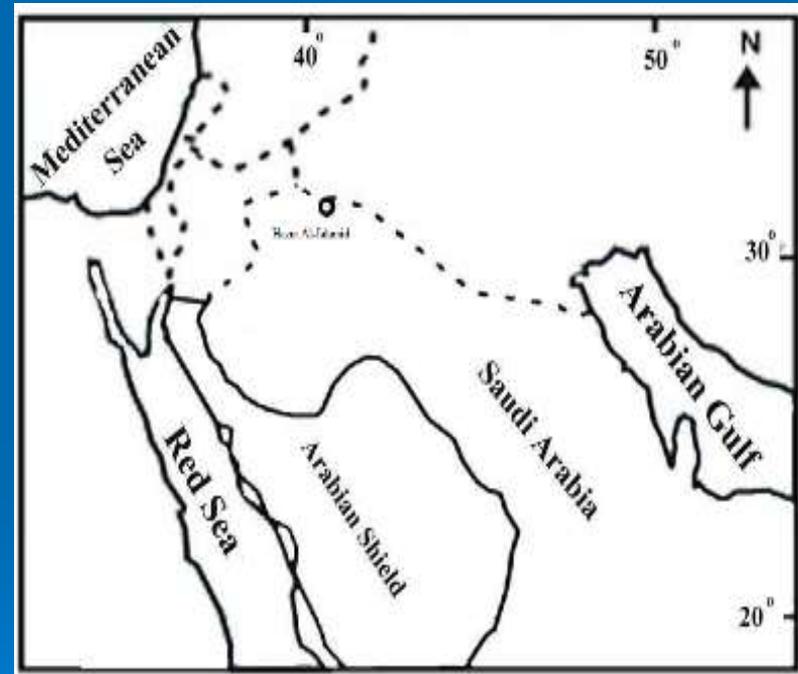
Advantages of the NAA Technique

- ❑ Samples for NAA can be liquid, solid, suspensions, or glass.
- ❑ NAA is a micro-analytical method, only a few milligrams of samples are required.
- ❑ NAA is a multi-element procedure. More than 30 elements can be measured in a given sample gamma-spectrum.
- ❑ NAA is fast in that many samples can be irradiated at a given time and counted later on a given decay schedule.
- ❑ NAA is unaffected by the presence of organic material in the sample, a significant problem in many types of chemical methods.



Samples Location

Al-Jalamid phosphate mine in the northeast of Saudi Arabia which started operation a few years ago, is one of the biggest mining locations in the Middle East region. It is planned to mine 12 million tons run of mine ore per year and produce about 4.5 million tons per year of phosphate concentrate for the next 20 years



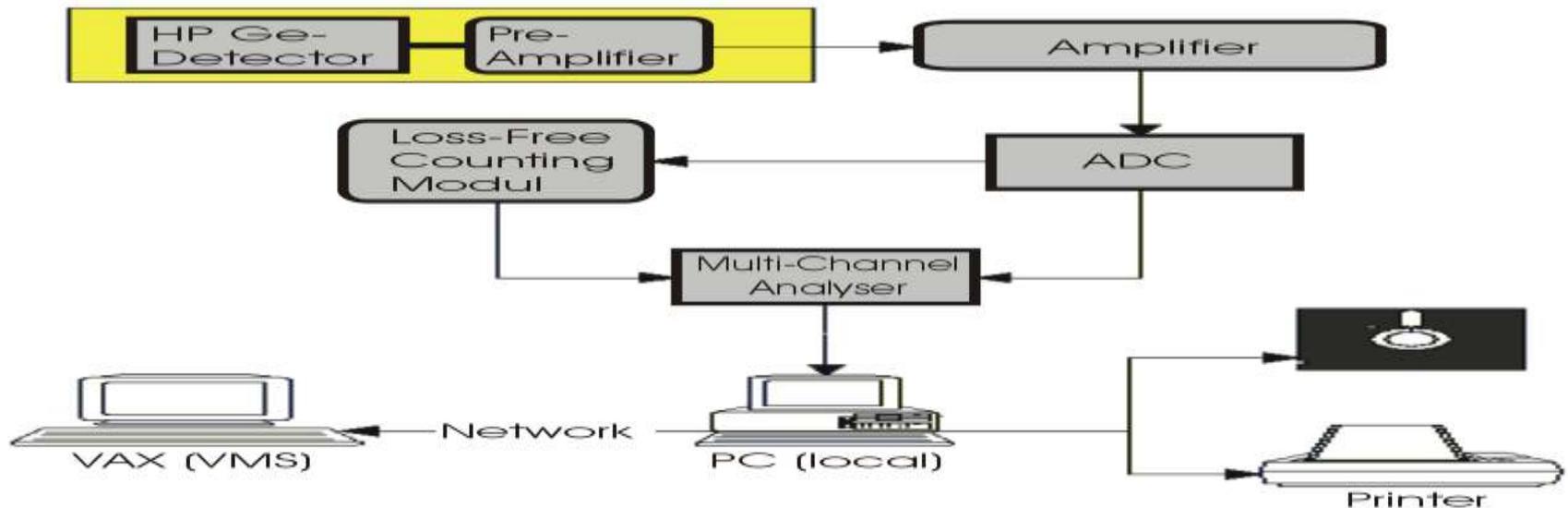


Samples Preparation

- ❑ Thirty representative phosphate rock samples were collected for investigation and analyzed.
- ❑ Samples are crushed to small pieces using a mechanical crusher. Then, the powdered samples are sieved using a standard set of sieves to a diameter range of less than 125 μm and greater than 63 μm .
- ❑ Every powdered sample is shaken using an electric shaker to be sure that the sample is homogenized.
- ❑ Polyethylene capsules filled with 100 mg of powdered samples are irradiated with thermal neutrons at the TRIGA Mainz research reactor.

Instrumentation

The gamma-ray spectrometer consists of a HPGe detector with its electronic circuit. The detector has the following specifications: energy resolution (FWHM) of 1.7 keV at 1.33 MeV gamma ray energy line of ^{60}Co , Peak to Compton ratio of 65.2, 29 % relative efficiency at 1.33 MeV gamma ray energy line of ^{60}Co . Bias voltage is +2000 V. The detector is connected to the following components: preamplifier, amplifier, ADC converter and MCA.



Nuclear properties of the rare-earth nuclides

Stable Isotopes	Abundance %	Activation product	Half-life	γ - energy, keV	Detection limit, ppm
La-139	99.9	La-140	40.2 h	1596	0.50
Ce-140	88.5	Ce-141	32.5 d	145	3.00
Pr-141	100	Pr-142	19.13h	1575.3	2.60
Nd-146	17.2	Nd-147	11 d	531	5.00
Eu-151	47.8	Eu-152	13.3y	1408	0.20
Sm-152	26.7	Sm-153	47 h	103	0.10
Gd-158	24.84	Gd-159	18.5h	363.5	1.80
Dy-164	28.2	Dy-165	2.33 h	94.7	0.20
Ho-165	100	Ho-166	26.9 h	80.6	0.13
Tm-169	100	Tm-170	130 d	84.3	0.10
Yb-168	31.6	Yb-169	32 d	198	0.20
Tb-159	100	Tb-160	72.1d	86.8	0.50
Lu-166	2.6	Lu-167	161 d	208	0.05
Er-170	14.9	Er-171	7.5 h	308.3	0.80

Irradiation cycles for Measuring REE by Instrumental neutron activation analysis

Polyethylene capsules filled with 100 mg from the samples together with standard reference materials were irradiated in the rotary specimen rack of the Mainz TRIGA research reactor by a thermal neutron

Irradiation time, h	Cooling time	Measuring time, S	Measured radionuclide
1	2 h	500	^{165}Dy , ^{142}Pr , ^{159}Gd , ^{171}Er
6	2 d	2000	^{140}La , ^{166}Ho , ^{170}Tm , ^{175}Yb , ^{177}Lu , ^{160}Tb
6	8 d	2000	^{141}Ce , ^{147}Nd , ^{153}Sm , ^{152}Eu

The average concentration of rare earth elementals in ppm in Hazm Al-Jalamid-phosphate samples

Element	Average
Ce	7.28
Dy	2.27
Er	1.88
Eu	0.44
Gd	2.26
Ho	0.60
La	14.01
Lu	0.28
Nd	7.98
Pr	1.83
Sm	1.69
Tb	0.35
Tm	0.28
Yb	1.75
Σ REE	42.89

Comparison between the concentration of rare earth elements in ppm in phosphate ore from different origin

Element	Florida	Morocco	Jordon	Kola	El-Jalamid Saudi Arabia	Um Waal Saudi Arabia	Hamrawin Egypt	El-Sibayia Egypt
	Ioneseu., 2000	Habashi, 2005	Habashi, 2005	Habashi, 2005	Present study			
La	600	300	92	22	14.83	39.1	31.2	41.6
Ce	200	180	200	2700	9.25	9.00	43.0	59.3
Pr	12	10	500	4500	1.83	4.13	6.84	25.5
Nd	100	90	14	350	< 5	25.0	18.0	30.3
Sm	85	15	100	1000	0.65	2.60	3.00	2.7
Gd	50	53	90	250	0.61	0.80	1.10	2.0
Eu	4	5	50	120	2.26	5.17	6.63	8.72
Tb	6	6	4	30	< 0.5	0.60	0.90	1.05
Dy	6	6	6	6	2.49	5.94	6.12	8.05
Ho	4	4	6	4	0.60	1.56	1.42	1.87
Er	5	5	4	5	1.88	4.86	4.18	5.63
Yb	6	6	6	6	1.66	4.70	3.50	4.67
Lu	5	7	7	7	0.79	1.68	2.03	2.42

Rare-earth elements in Egyptian granite by instrumental neutron activation analysis

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Rare earth elements content in geological samples from eastern desert, Egypt, determined by instrumental neutron activation analysis

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ORIGINAL ARTICLE

Uranium and rare earth elements in Hazm El-Jalamid phosphate, Saudi Arabia: concentrations and geochemical patterns comparison

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Conclusion

- ❑ The rare earth elements have high cross section for neutrons therefore, the sensitivity of neutron activation analysis provides a powerful tool for analysing rare earth elements in geological, and environmental systems.
- ❑ As in many cases nuclear techniques might not be available or might not be sufficiently sensitive, other non-nuclear techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) are also used.

THANK YOU

