Rare Earth Elements : Geochemistry and mineralogy

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Outline

- Definitions

- Chemical properties

- Geochemical significance

- Normalization of analytical data

- REE mineralogy

Definition of REE

- Lanthanides (La, Ce-Lu) + Y (+Sc)

- Divisions:

A. Light REE (LREE) = La – Eu

   Heavy REE (HREE) = Gd – Lu (+Y)

B. Light REE (LREE) = La – Nd

   Medium REE (MREE) = (Pm) – Ho

   Heavy REE (HREE) = Er – Lu (+Y)

Chemical properties of REE

- **Electron configuration** – general differentiation after electron occupancy of *4f* orbitals (inner shells), hence chemical behaviour coherency

- **Oxidation state** – in natural evironments most frequently REE^{3+}, but there is also ***Eu^{2+}***

  (in magmatic reductive environments) and ***Ce^{4+}***

  (in aqueous oxidation envronments)

- Ratios of *Eu^{2+}/Eu^{3+}* and *Ce^{4+}/Ce^{3+}* are dependant on temperature, pressure and redox potential (oxygen fugacity (*fO$_2$*)

REE electronic configuration → chem. properties

Symbol	Name	Z	Electronic configurat.
Y	Yttrium	39	$[Kr]\ 4d^1 5s^2$
La	Lanthanum	57	$[Xe]\ 5d^1 6s^2$
Ce	Cerium	58	$[Xe]\ 4f^2 6s^2$
Pr	Praseodyumium	59	$[Xe]\ 4f^3 6s^2$
Nd	Neodymium	60	$[Xe]\ 4f^4 6s^2$
(Pm)	Promethium*	61	$[Xe]\ 4f^4 6s^2$
Sm	Samarium	62	$[Xe]\ 4f^6 6s^2$
Eu	Europium	63	$[Xe]\ 4f^7 6s^2$
Gd	Gadolinium	64	$[Xe]\ 4f^7 5d^1 6s^2$
Tb	Terbium	65	$[Xe]\ 4f^9 6s^2$
Dy	Dysprosium	66	$[Xe]\ 4f^{10} 6s^2$
Ho	Holmium	67	$[Xe]\ 4f^{11} 6s^2$
Er	Erbium	68	$[Xe]\ 4f^{12} 6s^2$
Tm	Thulium	69	$[Xe]\ 4f^{13} 6s^2$
Yb	Ytterbium	70	$[Xe]\ 4f^{14} 6s^2$
Lu	Lutetium	71	$[Xe]\ 4f^{14} 5d^1 6s^2$

* No stable isotope in natural environments

→ Geochemical implications

- Due to similar electronic configuration this is a coherent group of elements with similar chemical behaviour (all REE tend to occur together in natural environments, with a mutual proportion of abundancies being a function of atomic number increase)

- Two processes imply REE applications in geological studies:

1. Fractionation of REE in igneous systems
2. Complexing of REE in aqueous systems

Ionic radii of REE

- Ionic radius – large ionic radii of REE are in range of around 1.00 Å and above; substitution mechanisms usually involve large cations like Ca^{2+}, Sr^{2+} and Na^+
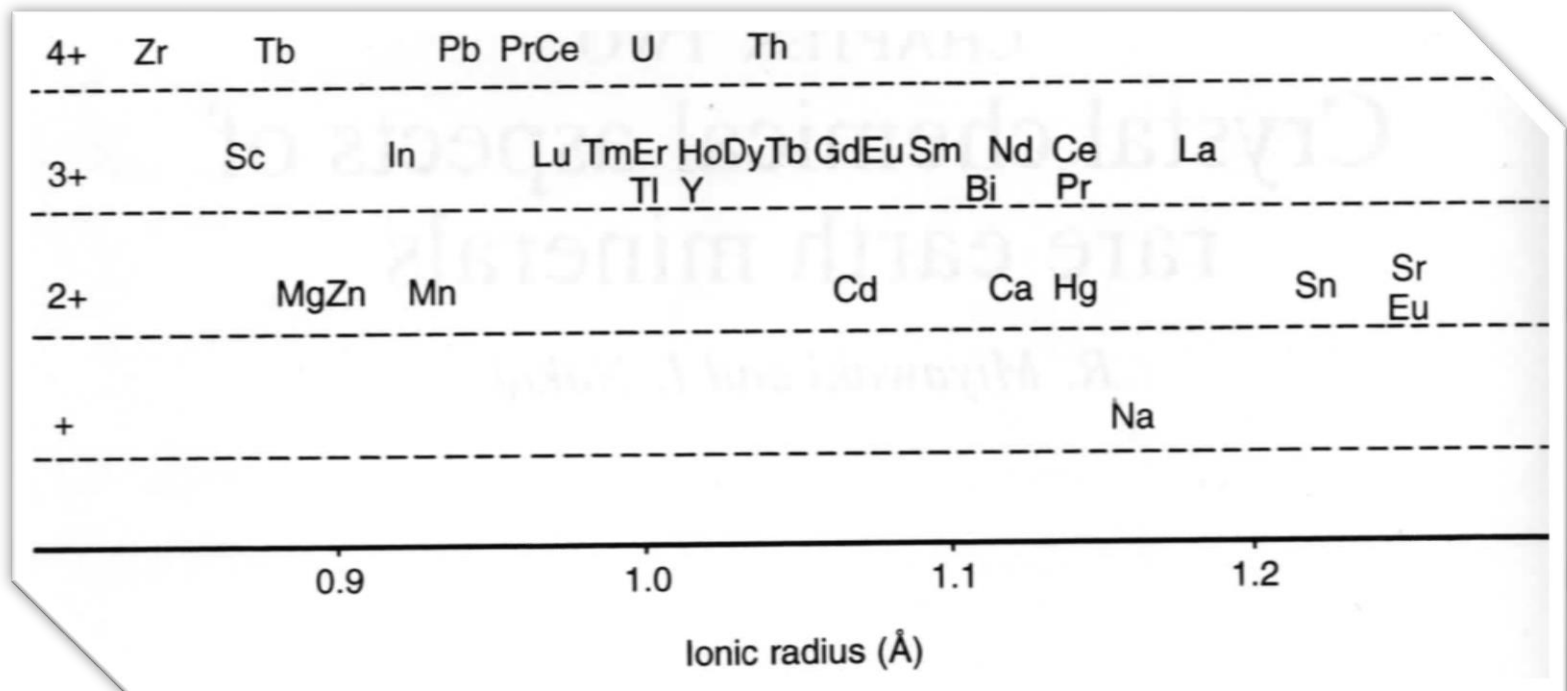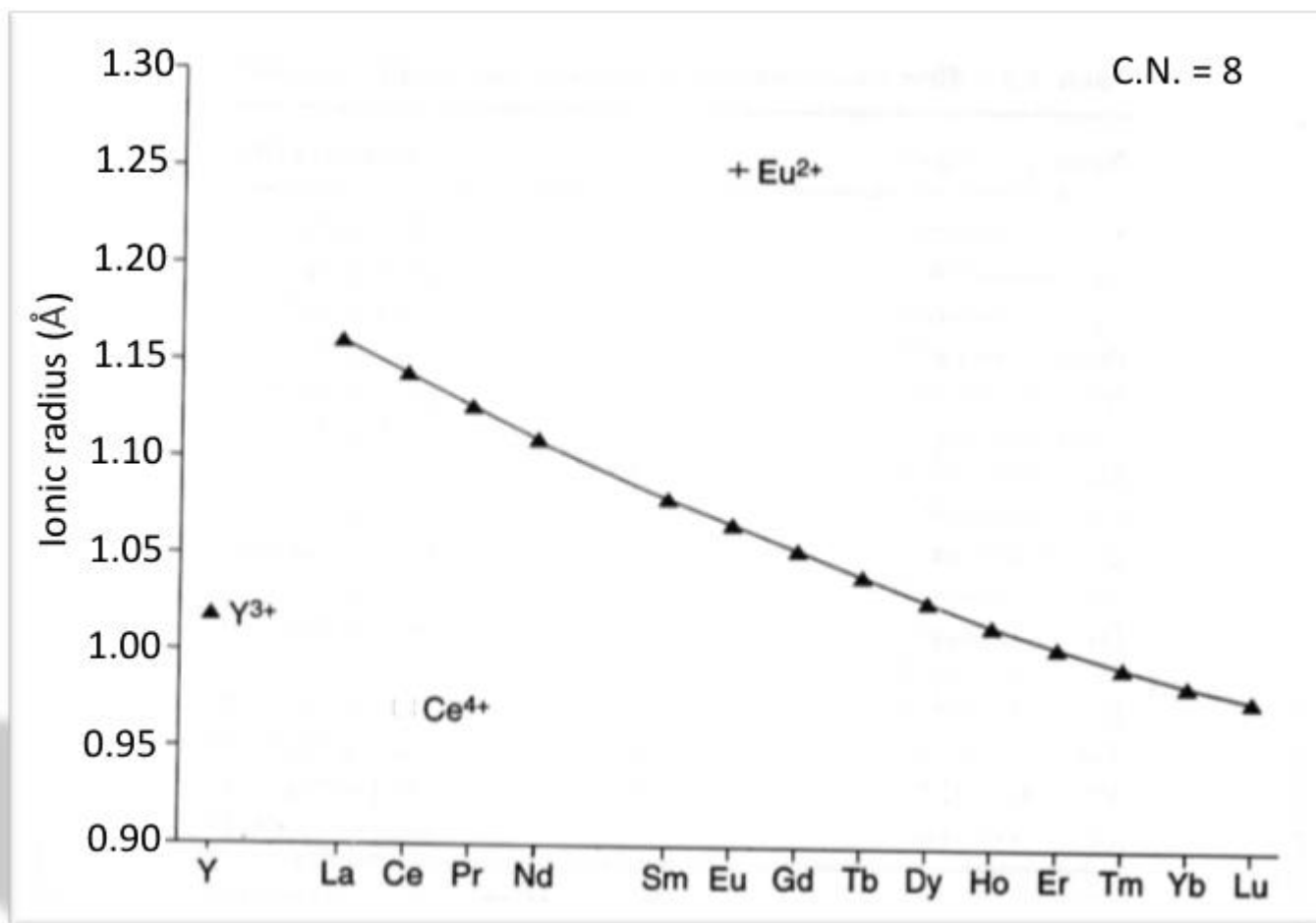

After Shannon & Prewit 1969, 1970

Diagram: Ionic radius vs. atomic number

After Shannon, 1978

Crustal abundances of REE

- Some REE abundances in the earth crust are very low, however, still higher than those of Au, Hg or In:

for seven REE abundances range 1-10 ppm, and for four 10-100 ppm (similar to Cu, Co and Zn); Ce is the most abundant

- There are various estimates on REE abundancies in the crust and mantle

Crustal abundances of REE in ppm

	Weaver and Tarney (1984)	Taylor and McLennan (1985)		Shaw et al. (1986)	Condie (1993)	
		Upper crust	Bulk continental crust		Map model	Restoration model
Y	13	22	20	21	29	30
La	27	30	16	32.3	25.6	27.3
Ce	55	64	33	65.6	55.7	59.3
Pr		7.1	3.9			
Nd	23	26	16	25.9	24.6	26.6
Sm	3.9	4.5	3.5	4.51	5.04	5.43
Eu	1.07	0.88	1.1	0.937	1.02	1.01
Gd		3.8	3.3	2.79	4.81	5.11
Tb	0.50	0.64	0.60	0.481	0.76	0.80
Dy		3.5	3.7			
Ho		0.80	0.78	0.623		
Er		2.3	2.2			
Tm	0.23	0.33	0.32			
Yb	1.46	2.2	2.2	1.47	2.33	2.36
Lu		0.32	0.30	0.233	0.43	0.43

Oscillation of REE abundances with *atomic number*

- There is a pronounced oscillation of REE abundancies with atomic number (***Oddo-Harkins effect*** – nuclei with even number are more stable and thus more abundant); abundances decrease with atomic number

- Thus the REE abundances in geological samples are normalized

- Different sets of normalization values are used depending on the type of the sample and purpose of the analyses: composite sample of chondrite, upper crust, North American shale composite (NASC) etc.

Normalization of REE abundances
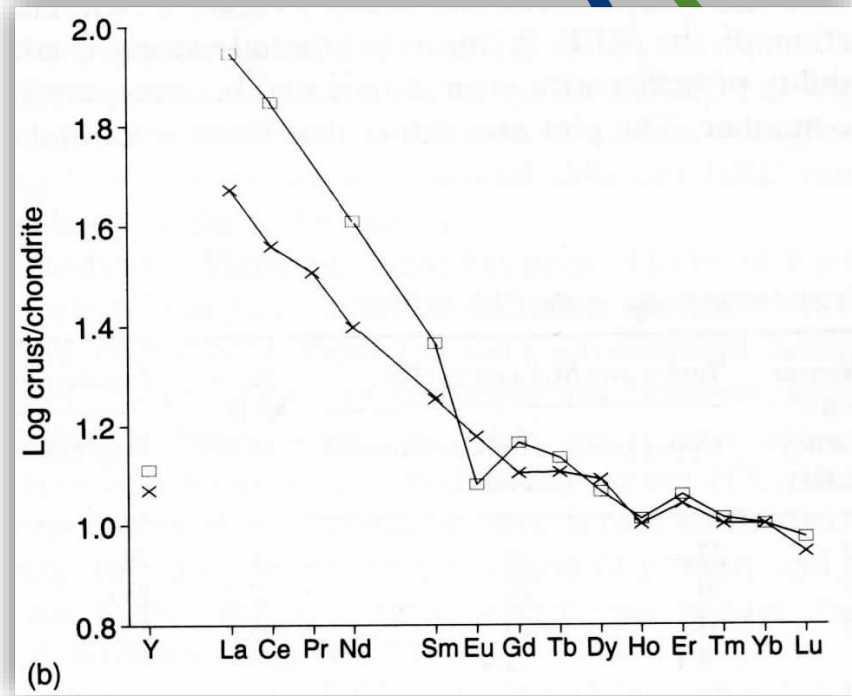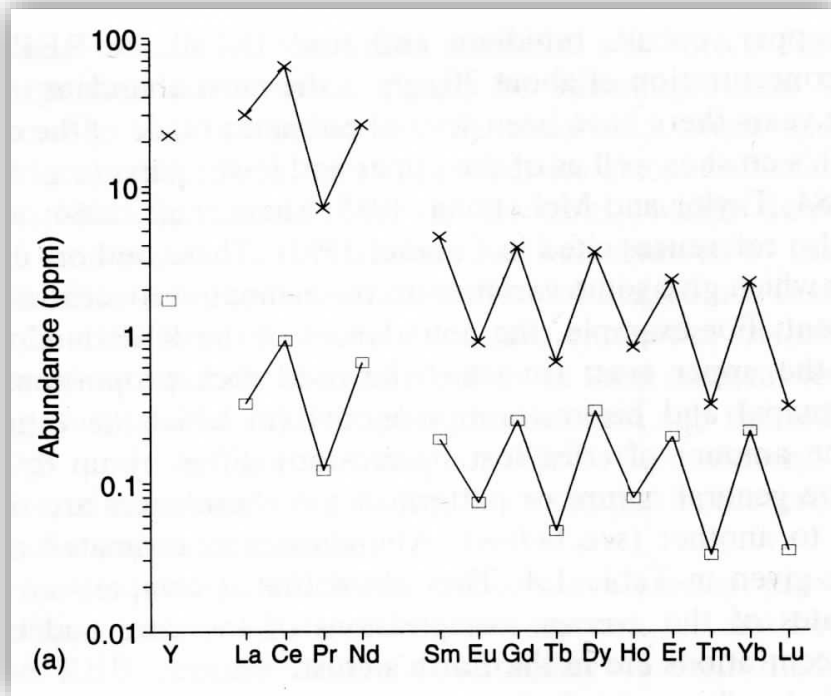
- REE Crust abundances: a) not normalized, b) chondrite normalized

(Taylor & McLennan, 1985)

REE in crystal structure of minerals

- Large ionic radius = higher coordination numbers (C.N. – number of atoms of one element surrounding an atom of another element).
- REE do not readily enter crystal structure of common rock forming minerals, so in cooling melt in magmatic systems REE tend to remain in melt (their partitioning coefficients, K_p, are low)

$$K_p = c_{REE\ (mineral)} / c_{REE\ (melt)}$$

REE fractionation in magmatic systems

- In primitive magma REE do not enter crystallizing minerals due to their small cationic sites (for instance, olivines, pyroxenes etc), so their concentration increases in successive melt fractions

    (***REE = incompatible elements***)

- In later stages of magmatic fractionation minerals with larger cation sites like zircon, titanite and apatite crystallize and incorporate REE as minor component in their structure

- REE become especially enriched in granite pegmatites, carbonatites and certain types of syenite

Partition coefficients vs. ionic radii

$Eu^{2+} \leftrightarrow Ca^{2+}$

Nash & Crecraft, 1985
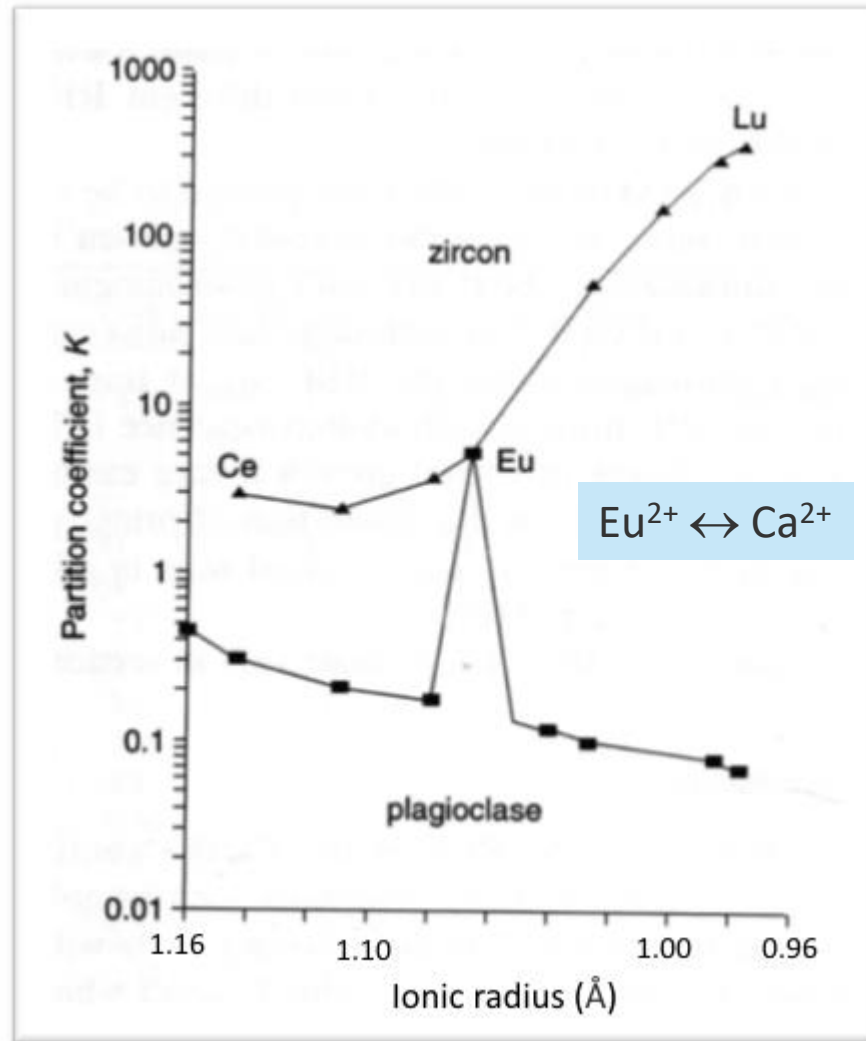
REE mobility in aqueous systems

- REE are quite mobile to a limited extent, though their compounds are of low solubility
- Mobility is influenced by: pH, Eh, ligand availability, and temperature
- In pH neutral and alkaline environments – complexing prevails
- In acidic systems – free REE ions are more stable
- Most important complexing agents: CO_3^{2-}, OH^-, F^-, Cl^-, SO_4^{2-}

$$REE^{3+}_{(aq)} + H_2O_{(l)} \leftrightarrow REE(OH)^{2+}_{(aq)} + H^+$$

Mineralogy of REE

- Due to their coherent chemical properties, all REE occur in a single mineral as a group, although usually single REE dominates over other REE in respect of abundancy

- Considering a content of REE in minerals, minerals could be classified in three groups:

1. ***Minerals with a very low concentration of REE*** – usually rock-forming minerals, with a variable LREE and HREE distribution
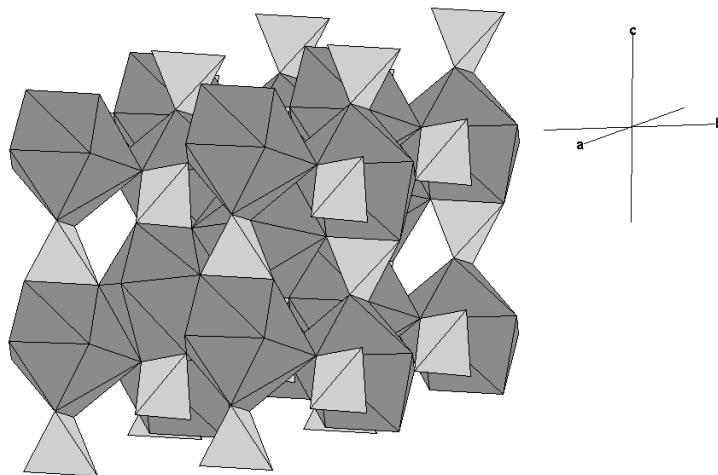
REE minerals

2. ***Minerals with a significant concentration of REE*** (more than 0.01 wt% of REE), with a characteristic REE distribution (zircon, apatite, titanite)

3. **Minerals with REE as major constituents** – ***REE minerals***

- Minerals with total atomic proportion of REE higher than of any other element at specific site in crystal structure (Bayliss & Levinson, 1988)

- REE minerals are named after Levinson (1966) nomenclature, which indicates dominant REE in a REE-mineral, for instance, monazite-(Ce), xenotime-(Y), bastnäsite-(Ce) etc.

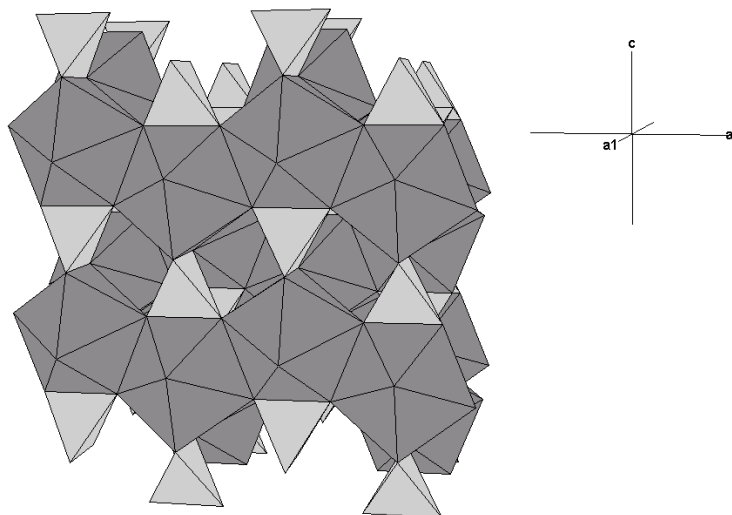# REE minerals - classes

- REE are very electropositive so they compounds are primarily:
  1. Oxides
  2. Phosphates
  3. Carbonates
  4. Halides
  5. Silicates

- Large ionic radii + higher ionic charge = higher coordination numbers (6-12 for REE, most common 8)

Example monazite-(Ce) and xenotime-(Y)

Monazite-(Ce)
LREE – C.N. 9

Xenotime-(Y)
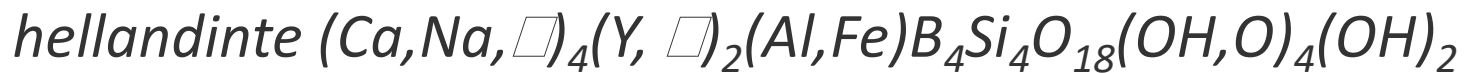HREE – C.N. 8

REE substitutions – frequent mechanisms

- In many minerals REE mutually substitute with Ca^{2+}, Na^+, Th^{4+} and often form solid solutions

- Main rules (McKay, 1989):

1. REE will replace main constituent in a crystal structure being the most similar in ionic radius,

2. Less energy-demanding substitutions are preferred, i.e. simple subsitutions that do not require coupled substituions (if possible, cations with same ionic charge will be preferred)

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Substitutions of REE

- LREE will generally replace Na^+ and Ca^{2+}
- HREE tend to substitute Th^{4+}

If needed, the different ionic charges of substituting cations will be compensated (Miyawaki & Nakai, 1996):

1. Sustitutions including structural vacancies

$$3Ca^{2+} \leftrightarrow 2REE^{3+} + \square$$

hellandinte $(Ca,Na,\square)_4(Y, \square)_2(Al,Fe)B_4Si_4O_{18}(OH,O)_4(OH)_2$

2. Substitution of two cations at one site (*apatite*)

$$2Ca^{2+} \leftrightarrow REE^{3+} + Na^+$$

Substitutions 2

3. Substitutions involving two structural sites (either cationic or anionic)

$$REE^{3+} + M^{n+} \leftrightarrow Ca^{2+} + M^{(n+1)+}$$

$$REE^{3+} + A^{n-} \leftrightarrow Ca^{2+} + A^{(n-1)-}$$

karbocernaite (Sr,Ce,Ba)(Ca,Na)(CO$_3$)$_2$

4. Chage of Fe valence

$$REE^{3+} + Fe^{2+} \leftrightarrow Ca^{2+} + Fe^{3+}$$
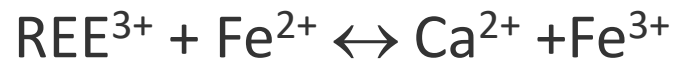
kalciogadolinite-(Y) YCaFe^{3+}Be$_2$Si$_2$O$_{10}$ and gadolinite-(Y) Y$_2$Fe^{2+}Be$_2$Si$_2$O$_{10}$
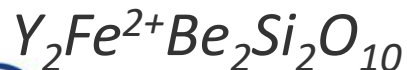
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