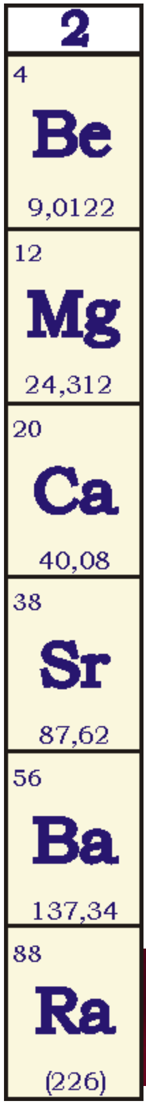
The metals from ‘earths’

Chemistry of the Group 2 metals:
The Alkali Earth Metals

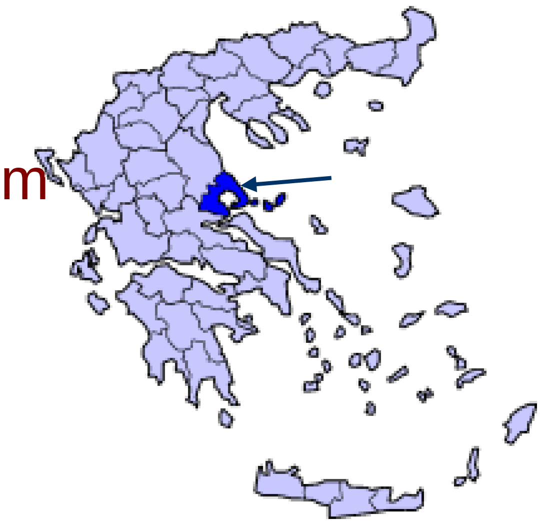
Occurrence

Like the Group 1 elements, the Group 2 metals occur only in minerals (never in elemental state)



Beryllos = beryl, 2 ppm (Earth Crust)

Magnesia = a district in Greece, 27 640 ppm



Calx (lat.) = lime, 46 600 ppm

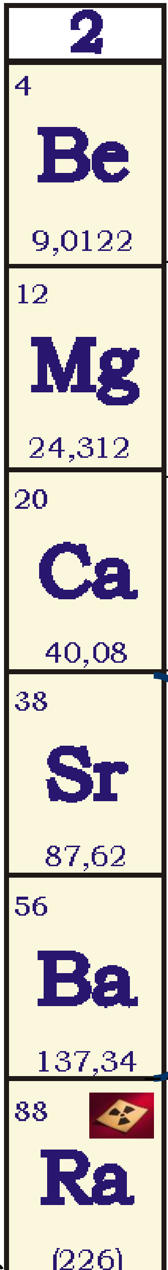
Strontian = a place in Scotland (mineral strontianite, $SrCO_3$), 384 ppm

Barys (gr.) = heavy, 390 ppm

Radius (lat.) = ray, ~10^{-6} ppm

Data from J. Emsley 'The Elements' Oxford: Claredon Press, 1989

Isolation



Electrolysis of $BeCl_2$ obtained from beryl ($Be_3Al_2Si_6O_{18}$)

Electrolysis of $MgCl_2$ obtained from dolomite, $(Mg,Ca)CO_3$:

$$(Mg,Ca)CO_3 + 2HCl \rightarrow 0.5MgCl_2 + 0.5CaCl_2 + CO_2\uparrow + H_2O$$

Electrolysis of $CaCl_2$ obtained from calcite and/or dolomite or more frequently using termite process (see below).

Electrolysis of MCl_2 (M = Sr, Ba) or reduction of metal oxides with Al (termite process):

$$3MO + 2Al \xrightarrow{\Delta} 2M + Al_2O_3 \text{ (termite process)}$$

Post-processing of uranium ores

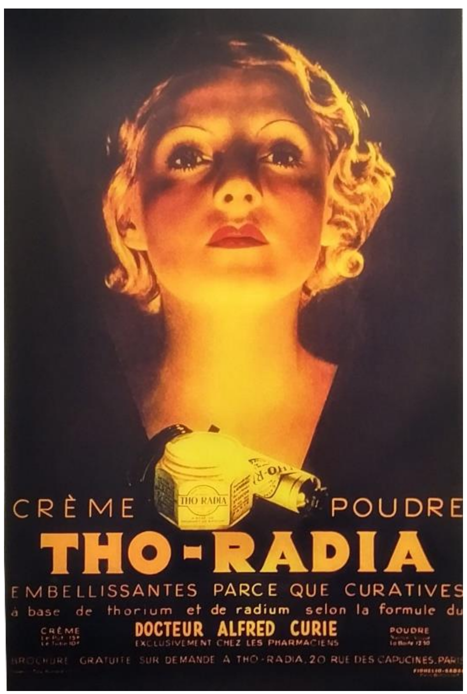
Physical properties

- Typical metals: silvery solids, conduct electricity.
- Compared to alkali metals, alkali earth metals are much harder and have higher melting and boiling points (why?).
- Mg shows some anomalies in the trends:

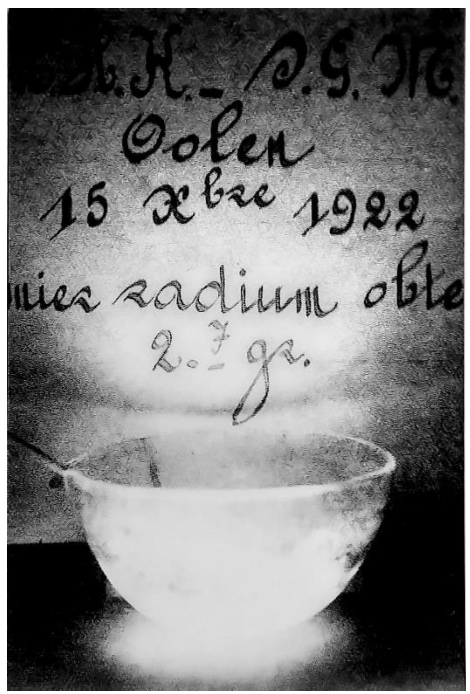
Property	Be	Mg	Ca	Sr	Ba
Atomic number, Z	4	12	20	38	56
Ground state electronic config.	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$
Melting point (K)	1560	923	1115	1040	1000
Boiling point (K)	≈3040	1380	1757	1657	1913
$\Delta_{sub}H^o$ (kJ/mol)	324	146	178	164	178
I_1 (kJ/mol)	899.5	737.7	589.8	549.5	502.8
I_2 (kJ/mol)	1757	1451	1145	1064	965.2
$\Delta_{hyd}H^o$ (kJ/mol)	-2500	-1931	-1586	-1456	-1316
Metallic radius (pm)	112	160	197	215	214
Ionic radius (pm)	27	72	100	126	124
$E^o_{M+/M}$ (V)	-1.85	-2.37	-2.87	-2.89	-2.90

Nuclear characteristics

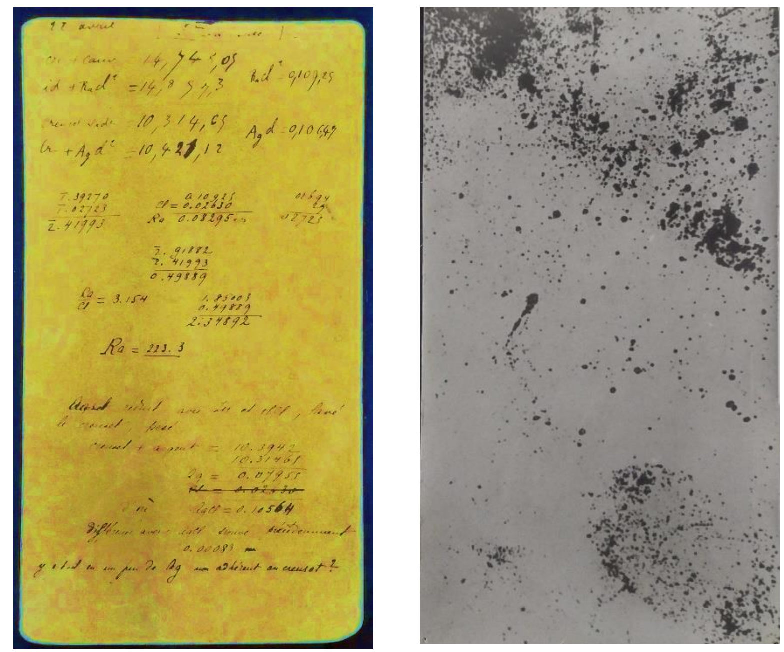
- Beryllium-9, the only stable Be isotope, is formed by spallation (fragmentation) by galactic cosmic ray bombardment (see Li in Group 1).
- Radium: all isotopes (four occurring in nature) are radioactive.



A magazine ad for radium-containing face cream and powder



A photograph of 2.7g of $RaBr_2$ taken in its own light



A page form M. Curie notebook showing the calculation of radium's atomic weight (left) and the same page showing the areas with radioactive material

Chemical properties & reactivities

- Oxidation state/number **+2**.
- Reactive metals (but less reactive than the Group 1 metals), strong reducing agents.
- Standard reduction potentials: remain almost constant for Ca-Ra.
- Heavier group members readily combine directly with many other elements.
- Reactivity increases going down the group:
  - Reactivity with water: Be is almost unaffected by steam (passivation), Mg reacts with steam, Ca reacts with cold water and Sr & Ba react almost as violently as Na and K.
  - All react with acids liberating H_2 and giving salts.
  - Can be combined directly with almost all elements (O_2, N_2, halogens, carbon, etc.).
- The coordination chemistry of light Group 2 elements is richer than the Group 1 elements.

Reactivity: Details

- All except Be react directly with gaseous H_2 giving hydrides:

$$M\ (s) + H_2\ (g) \xrightarrow{\Delta} MH_2\ (s)$$

  - Does not work for BeH_2 since $\Delta_f H$ (BeH_2) ~ 0 kJ/mol, Mg only under high H_2 pressures.

- All react with carbon producing ionic carbides:

$$M\ (s) + 2\ C\ (s) \xrightarrow{\Delta} MC_2\ (s)$$

  - Be gives only Be_2C and *not* expected BeC_2

- All react with O_2, N_2 and halogens:

$$M\ (s) + 1/2\ O_2\ (g) \xrightarrow{\Delta} MO\ (s) \quad \text{(oxides)}$$

$$3M\ (s) + N_2\ (g) \xrightarrow{\Delta} M_3N_2\ (s) \quad \text{(nitrides)}$$

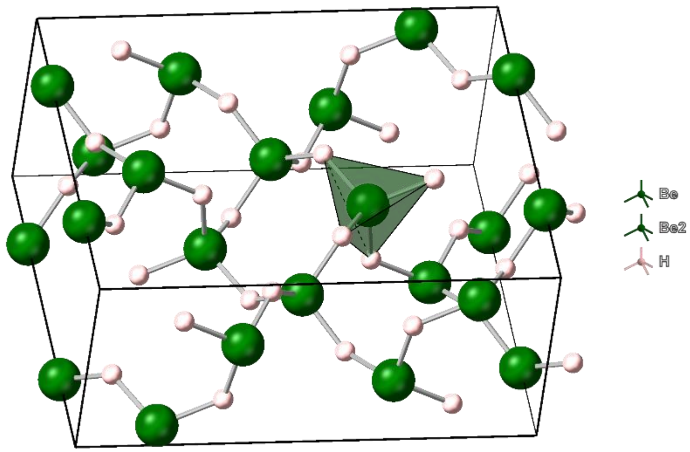
$$M\ (s) + X_2\ (g) \xrightarrow{\Delta} MX_2\ (s) \quad \text{(halides)}$$

M = Be - Ra

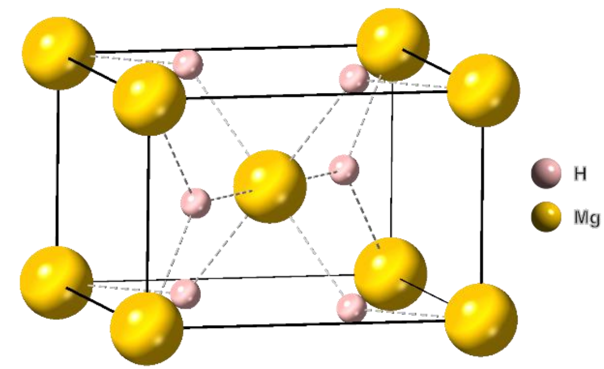
(X = F, Cl, Br, I)

Note: Ba forms **peroxide**, *not* oxide, with O_2

Hydrides (MH_2)



A network structure of BeH_2



Rutile (TiO_2) –type structure of MgH_2

- Ca-Ra have more complex structures.
  - Compare this diversity in structures for Group 2 hydrides with the structure of Group 1 hydrides
- Like hydrides of the Group 1 metals, all MH_2 react with H_2O liberating H_2 and forming $M(OH)_2$:

$$MH_2\ (s) + H_2O \longrightarrow H_2\ (g) + M(OH)_2$$

  - CaH_2 is often used as drying agent for organic solvents that do not have acidic hydrogen atoms.
- MgH_2 and CaH_2 are also useful reducing agents

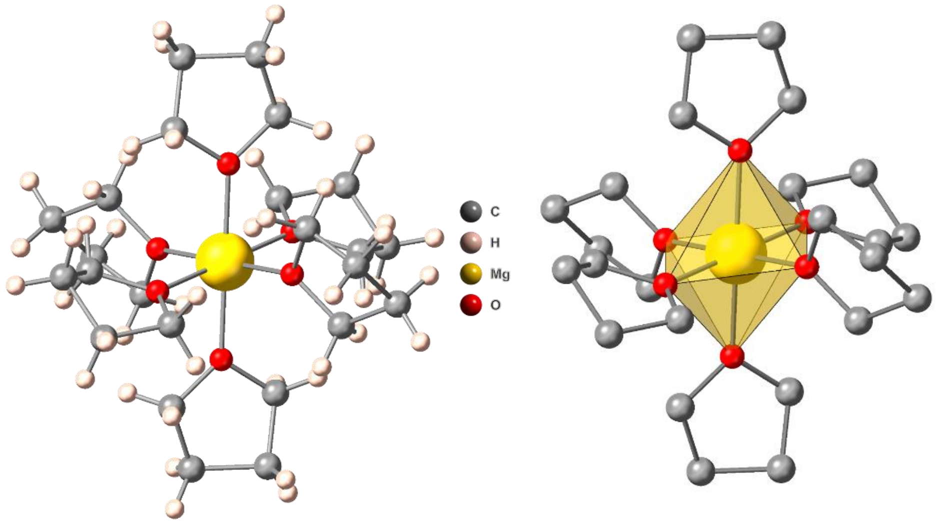
Halides (MX_2)

- Structural variety is even more obvious for halides
  - Note deviation from VSEPR theory for gas phase molecules!
  - Compare with halides of Group 1 elements

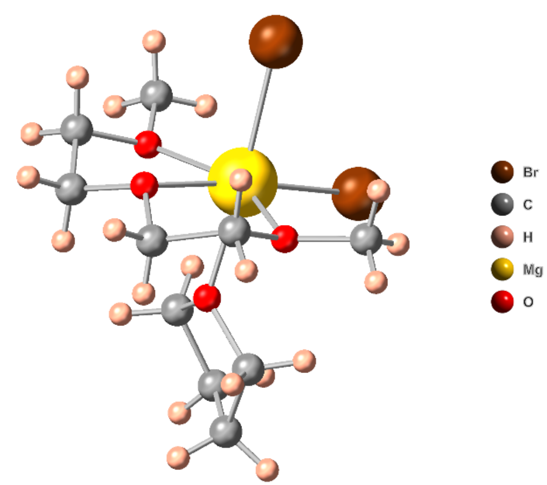
	Phase	F	Cl	Br	I
Be	**Solid**	β-SiO_2	Chain	Chain	Chain
	Gas	Linear	Linear	Linear	Linear
Mg	**Solid**	TiO_2	$CdCl_2$	CdI_2	CdI_2
	Gas	Linear	Linear	Linear	Linear
Ca	**Solid**	CaF_2	Deformed TiO_2	Deformed TiO_2	CdI_2
	Gas	*Bent*	Linear	Linear	Linear
Sr	**Solid**	CaF_2	Deformed TiO_2	$PbCl_2$	SrI_2
	Gas	*Bent*	*Bent*	Quasi-linear	Linear
Ba	**Solid**	CaF_2	$PbCl_2$	$PbCl_2$	$PbCl_2$
	gas	*Bent*	*Bent*	*Bent*	*Bent*

Halides (MX_2) – cont.

- All halides are hygroscopic and hydrates are well-known
- Be and Mg halides are soluble in organic solvents that can act as Lewis bases (such as ethers):
  - Compare with Group 1 with crown ethers and cryptands

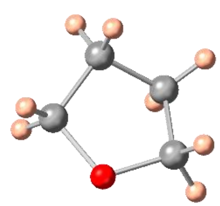


Structure of $[Mg(THF)_6]^{2+}$ cation

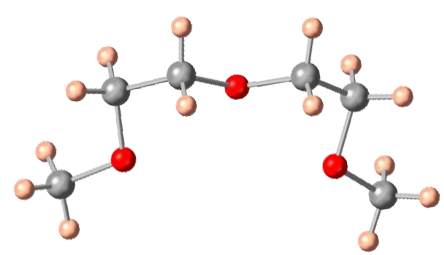


Structure of $[MgBr_2(diglyme)(THF)_6]$

THF = tetrahydrofurane (C_4H_8O)



diglyme = a linear polyether ($C_6H_{14}O_3$)



Nitrides and Carbides

- Both nitrides and carbides react with water.
  - Nitrides and carbides of the heavier Group 2 elements are more ionic and react with water violently.
- Reaction of nitrides with H_2O produces ammonia and metal hydroxide:

$$M_3N_2 + 6H_2O \longrightarrow 3M(OH)_2 + 2NH_3$$

  - This acid–base reaction shows that f*ormally* nitrides can be considered salts of ammonia, NH_3.
- Reaction of carbides with H_2O produces acetylene (however Be_2C gives methane):

$$MC_2 + H_2O \longrightarrow M(OH)_2 + C_2H_2$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

  - Similarly, as above for nitrides, the acid–base reactions show that MC_2 carbides can be formally considered as slats of acetylene (HC≡CH, and are sometimes called *acetylides*) while M_2C salts of methane.

Oxides & hydroxides

- All oxides are known
- Old name for MgO and CaO is ‘earths’
- All except BeO are purely basic oxides
- BeO is insoluble in water, MgO is slowly converted to $Mg(OH)_2$ – a *weak-ish* base, CaO, SrO and BaO react rapidly to produce $M(OH)_2$ (M= Ca, Sr, Ba), all strong bases
- $Be(OH)_2$ is insoluble and can be precipitated:

$$Be^{2+}(aq) + 2OH^{-}(aq) \longrightarrow Be(OH)_2(s)$$

- BeO and $Be(OH)_2$ are *amphoteric* (they behave as both acids and bases thus react *with* both acids and bases):

$$\underset{\textit{acid}}{Be(OH)_2(s)} + \underset{\textit{base}}{2OH^{-}(aq)} \longrightarrow \underset{\textit{beryllate}\text{ salts}}{[Be(OH)_4]^{2-}(aq)}$$

$$\underset{\textit{base}}{Be(OH)_2(s)} + \underset{\textit{acid}}{2HX(aq)} \longrightarrow \underset{\textit{berylliumum}\text{ salts}}{BeX_2(aq) + 2H_2O}$$

Aqueous solutions

- The composition of M^{2+} (aq):

Be^{2+} (aq) = $[Be(H_2O)_4]^{2+} + H_2O \longrightarrow [Be(H_2O)_3(OH)]^{+} + H_3O^{+}$

  - Various condensation species can be formed from $[Be(H_2O)]^{2+}$, for example:

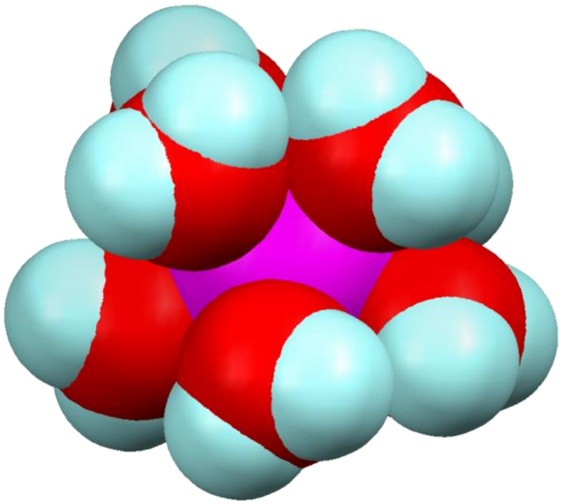
$$4[Be(H_2O)_4]^{2+} + 2H_2O \longrightarrow 2[(H_2O)_3Be\text{-}O\text{-}Be(H_2O)_3]^{2+} + 4H_3O^{+}$$

Mg^{2+} (aq) = $[Mg(H_2O)_6]^{2+}$ ⟵ Octahedral structure

Ca^{2+} (aq) = $[Ca(H_2O)_n]^{2+}$ $n \geq 6$

M^{2+} (aq) = $[M(H_2O)_8]^{2+}$ M= Sr, Ba, Ra

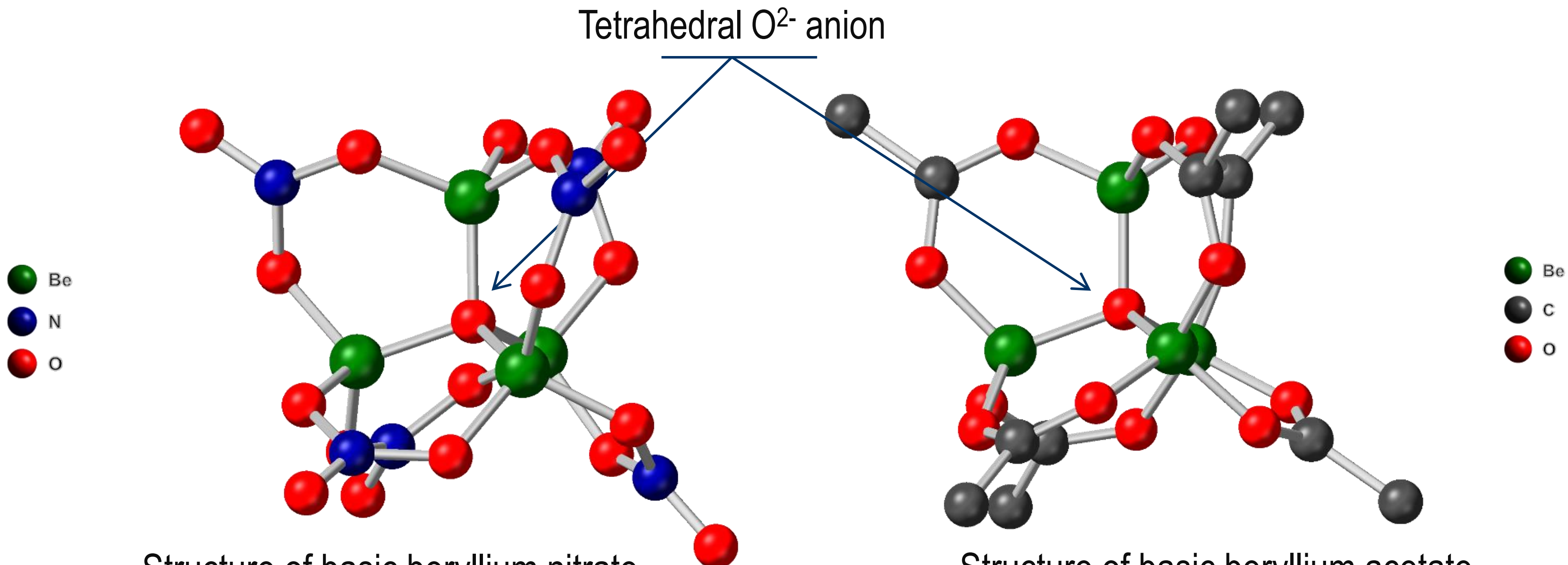
Spacefilling of $[Sr(H_2O)_8]^{2+}$ structure



- The number of water molecules surrounding a cation in aqueous solutions (a primary hydration sphere) increases going down the group (follows the increase in cationic radius!).

Oxosalts

- Beryllium acetate and nitrate have very specific structures:



Structure of basic beryllium nitrate

$[Be_4(O)(NO_3)_6]$

Structure of basic beryllium acetate

$[Be_4(O)(O_2CCCH_3)_6]$

- Sulfates are commonly encountered in laboratory (i.e. anhydrous $MgSO_4$ is used as drying agent).
- Important sulfate is also gypsum ($CaSO_4 \times 2H_2O$)

Oxosalts (cont.)

- Carbonates are not soluble in water and all (except Be) are important natural resources.
- $CaCO_3$ occurs naturally as calcite or aragonite (less stable polymorph); $MgCO_3$ is magnesite while dolomite is a mixed carbonate $(Mg,Ca)CO_3$.
- Water hardness:
  - *Temporary water hardness* – due to dissolved Ca and Mg hydrogencarbonates (removed when water is boiled):

$$M^{2+}\,(aq) + 2\,HCO_3^-\,(aq) \xrightarrow{\Delta} MCO_3\,(s) + CO_2\,(g) + H_2O\,(l)$$

  - *Permanent water hardness* – due to other Mg and Ca salts dissolved in water (require more processing to remove).
- Mg – Ba carbonates are thermally unstable and decompose to MO and CO_2.

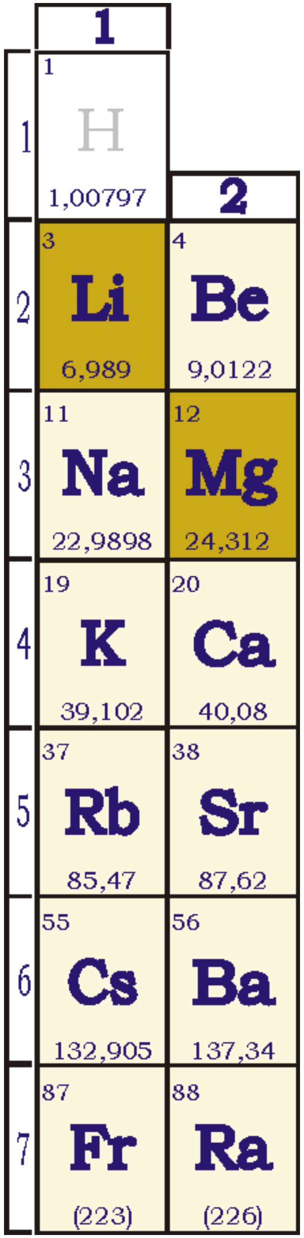
Magnezite ($MgCO_3$)

Strontianite ($SrCO_3$)

Calcite & beryl (green)

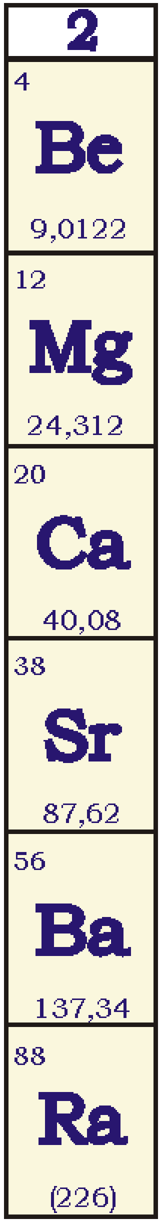
Photos: www.webmineral.com

Diagonal relationships



- The chemistry and properties of Li resemble somewhat the chemistry and properties of Mg (diagonally below):
  - Rate of reaction with H_2O;
  - In reaction with O_2 both give expected oxides;
  - Both Li and Mg give sparingly soluble hydroxides;
  - Both LiOH and $Mg(OH)_2$ are significantly weaker bases compared to the hydroxides of heavier elements;
  - Both Li^+ and Mg^{2+} are more strongly hydrated than are ions of the later Group 1 and Group 2 elements;
  - LiF and MgF_2 are sparingly soluble.
- This type of relationship between two elements lying on a diagonal is called *diagonal relationship.*

Overview



- Occurrence and isolation;
- Nuclear properties;
- Chemical and physical properties;
- Reactivity (keep in mind distinctiveness of Be*!*);
  - With H_2 (structure of BeH_2);
  - With X_2 (halogens, structures in gas phase, structure of $BeCl_2$);
  - With O_2;
  - With C (carbides, note Be_2C, reactivity with water);
  - With N_2 (reactivity with water);
- Hydroxides and their properties;
- Structure of Be oxo salts;
- Carbonates: importance, thermal stabilities and water hardness
- The Group 2 ions in aqueous solutions;
- Diagonal relationships.

Readings and problems

- Readings (either 6^{th} or 7^{th} edition)
  - **Chapter 12**: The Group 2 – The alkali earth metals (but skip sections 12.12 and 12.13)
  - Pay attention to Box 12.5 (12.4 in 6^{th} edition)
- Problems
  - 6^{th} edition:
    - Examples and Self-tests: 12.1, 12.2, 12.3, 12.4, 12.5
    - End-of-chapter exercises: 12.1, 12.2, 12.3, 12.4, 12.6, 12.11
  - 7^{th} edition:
    - Examples and Self-tests: 12.1, 12.2, 12.3, 12.4, 12.5, 12.6, 12.7
    - End-of-chapter exercises: 12.1, 12.2, 12.3, 12.4, 12.5, 12.7, 12.8, 12.9, 12.10, 12.13, 12.16, 12.17.
- A bit more practice:
  - Write balanced equation for the reaction between water and all Group 2 (i) oxides, (ii) nitrides and (iii) carbides
  - Find $MgCl_2$ and $MgBr_2$ on the Ketelaar triangle and use the location to rationalize their structures.

Readings and problems (cont.)

- To determine the atomic weight of radium, Marie Curie dissolved a sample of $RaCl_2$ in water and then precipitated all chloride as AgCl. Repeat her calculations knowing that she obtained 0.08890 g of AgCl from 0.09192 g of $RaCl_2$. At that time the atomic weight of Cl was set at 35.4 and that of Ag was 107.8.

- If you want to explore more
  - Epsom salt
  - Calcium carbonate polymorphs
  - Determining water hardness using complexometric titrations
  - Marie Cuire
  - Solvent drying agents