# 2. Alkaline Earth Metals

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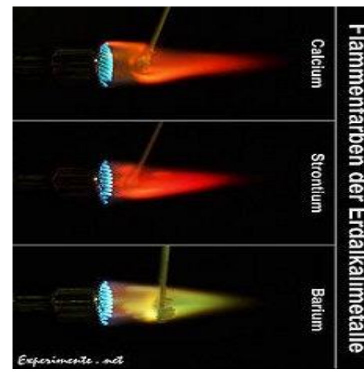



| | *Group 2 or IIA* |
|---|---|
| 4 Be | *1797* |
| 12 Mg | *1755* |
| 20 Ca | *1808* |
| 38 Sr | *1790* |
| 56 Ba | *1808* |
| 88 Ra | *1898* |

*„Alkaline earth metals“*

# 2.1 Occurence

## Abundance in the Earth's Crust

**Be: $2.7 \cdot 10^{-4}$%, <u>Mg: 1.9%, Ca 3.4%,</u> Sr: $3.6 \cdot 10^{-2}$%, Ba: $4.0 \cdot 10^{-2}$%**

| | | |
|---|---|---|
| **<u>Beryllium (beryllos)</u>** | $Be_3Al_2[Si_6O_{18}]$ | Beryl, emerald, aquamarine |
| *greek: Beryll* | $Al_2[BeO_4]$ | Chrysoberyl |
| | $Be_2SiO_4$ | Phenakite |
| **<u>Magnesium (magnesia)</u>** | $(Ca,Mg)CO_3$ | Dolomite |
| *town in Asia Minor* | $(Mg,Fe)[SiO_4]$ | Olivine |
| | $Mg_3(OH)_2[Si_4O_{10}]$ | Talc |
| | $MgAl_2O_4$ | Spinel |
| | Meerwasser | 1,3 g/l |
| **<u>Calcium (calx)</u>** | $CaSO_4$ | Gypsum |
| *latin: lime* | $CaCO_3$ | Calcite, aragonite |
| | $CaF_2$ | Fluorite |
| | $Ca_5(PO_4)_3(OH,F)$ | Apatite |
| **<u>Strontium (strontian)</u>** | $SrSO_4$ | Cölestine |
| *Place in Scotland* | $SrCO_3$ | Strontianite |
| **<u>Barium (barys)</u>** | $BaSO_4$ | Barite |
| *greek: heavy* | $BaCO_3$ | Witherite |

# 2.2 Properties

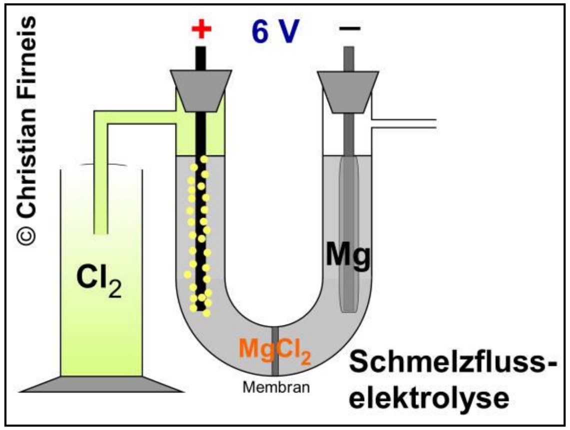
**All Elements of the Group are Typical Metals and Exist in the Oxidation State +II**

| | Be | Mg | Ca | Sr | Ba |
|---|---|---|---|---|---|
| Atomic number | 4 | 12 | 20 | 38 | 56 |
| Electronic configuration | [He] $2s^2$ | [Ne] $3s^2$ | [Ar] $4s^2$ | [Kr] $5s^2$ | [Xe] $6s^2$ |
| Electronegativity | 1.5 | 1.2 | 1.0 | 1.0 | 1.0 |
| Ionisation energy [eV] | 9.3 | 7.6 | 6.1 | 5.7 | 5.2 |
| Ionic radius $Me^{2+}$ for CN 6 [pm] | 59 | 86 | 114 | 132 | 149 |
| Melting point $T_m$ [°C] | 1287 | 650 | 842 | 777 | 727 |
| Boiling point $T_b$ [°C] | 2470 | 1093 | 1484 | 1412 | 1845 |
| Density [g/cm$^3$] | 1.90 | 1.74 | 1.55 | 2.63 | 3.50 |
| Flame colouring | UV/NIR | whitish | brick red 622 nm | crimson red 605 nm | green 514 + 524 nm |

- Beryllium exhibits different phys. properties than the other alkaline earth metals
- The combustion of the metals leads to oxides. With Ba also peroxides ($BaO_2$) originate
- With nitrogen the nitrides $Me_3N_2$ are formed
- The alkaline character of the hydroxides increases with increasing atomic number
- The more alkaline the metal the more stable are the corresponding carbonates and nitrates

# 2.3 Synthesis

## By Fused-Salt Electrolysis or by Chemical Reduction




**Beryllium**

Via reduction of $BeF_2$ with Mg in graphite crucibles at 1300 °C

$BeF_2(s) + Mg(s) \rightarrow Be(s) + MgF_2(s)$

**Magnesium**

By fused-salt electrolysis of $MgCl_2$ at 700 – 800 °C

$MgCl_2(l) \rightarrow Mg(s) + Cl_2(g)$

Anhydrous $MgCl_2(s)$ can be obtained through $MgO(s) + Cl_2(g) + C(s) \rightarrow MgCl_2(s) + CO(g)$

**Calcium, Strontium**

By fused-salt electrolysis of the chlorides mixed with the fluorides (eutectic)

**Barium**

By reduction of BaO with Al or Si at 1200 °C in vacuum

$3\ BaO(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 3\ Ba(g)$

$3\ BaO(s) + Si(s) \rightarrow BaSiO_3(s) + 2\ Ba(g)$

BaO is obtained by thermal decomposition of $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)\uparrow$

# 2.4 Applications

**Beryllium**

- Low neutron absorption cross-section → moderator and reflector for neutrons
- Low density → emission windows for x-ray sources
- Be-Cu-alloys → good conductivity and a hardness comparable to that of steel
- Be-Ni-alloys → watch spring and surgical instruments

**Magnesium**

- Density = 1.74 $g/cm^3$ → Mg-alloys as light metals in the aviation and automotive industry
- Energy source of the future?: $2\ Mg(s) + O_2(g) \rightleftharpoons 2\ MgO(s)$ $\Delta H^0_R = -1204$ kJ/mol

**Calcium, Strontium and Barium**

- Calcium is used as a reduction agent in metallurgy
- Ba is used as getter material in cathode ray tubes and discharge lamps
- The mixed oxide BaO/SrO/CaO reacts with tungsten at high temperatures and is used as thermionic electron emitter:

  $BaO + W \rightarrow Ba_3WO_6 + 3\ Ba$ (efficient thermal $e^-$ emitter)
- BaO is used as a additive in glasses to increase the cross-section for x-rays
- CaO shows white ⇒ thermo-luminescence "limelight"

# 2.5 Alkaline Earth Metal Salts

**The Covalent Character of the Salts and Their Solubility Depends Strongly on the Ionic Charge Density (ICD) of the Cations**

| Ion | CN | Radius [pm] | ICD [C/mm³] |
|---|---|---|---|
| $Be^{2+}$ | 4 | 41 | 1100 |
| | 6 | 59 | 370 |
| $Mg^{2+}$ | 4 | 71 | 210 |
| | 6 | 86 | 120 |
| $Ca^{2+}$ | 6 | 114 | 52 |
| | 8 | 126 | 38 |
| $Sr^{2+}$ | 6 | 132 | 33 |
| | 8 | 140 | 28 |
| $Ba^{2+}$ | 6 | 149 | 23 |
| | 8 | 156 | 20 |

↑ Covalent character of the salts

↑ Solubility of the sulphates

↓ Solubility of the hydroxides

Compounds with Mg and, to a even larger degree, with Be show a distinct covalent character:

- Mg forms Grignard-compounds R-MgBr (R = alkyl)
- Be forms coordinative bonds, e. g. in $[Be(H_2O)_4]^{2+}$ and $(BeCl_2)_n$

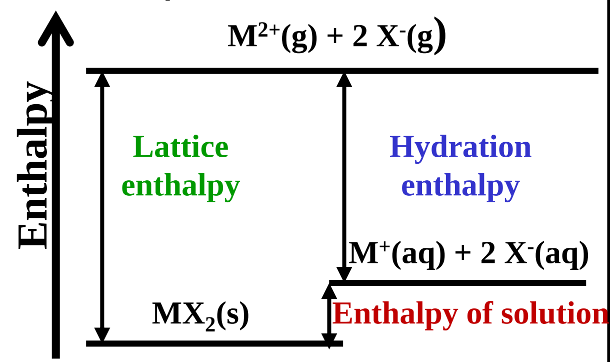
# 2.5 Alkaline Earth Metal Salts

## The Hydration of the Alkaline Earth Cations Depends on the Ionic Charge Density

| Ion | Chloride | Nitrate | Sulphate |
|---|---|---|---|
| $Mg^{2+}$ | $MgCl_2 \cdot 6H_2O$ | $Mg(NO_3)_2 \cdot 6H_2O$ | $MgSO_4 \cdot 7H_2O$ |
| $Ca^{2+}$ | $CaCl_2 \cdot 6H_2O$ | $Ca(NO_3)_2 \cdot 4H_2O$ | $CaSO_4 \cdot 2H_2O$ |
| $Sr^{2+}$ | $SrCl_2 \cdot 6H_2O$ | $Sr(NO_3)_2 \cdot 4H_2O$ | $SrSO_4$ |
| $Ba^{2+}$ | $BaCl_2 \cdot 2H_2O$ | $Ba(NO_3)_2$ | $BaSO_4$ |

**Enthalpy of solution = hydration enthalpy – lattice enthalpy**

**Entropy of solution = hydration entropy – lattice entropy**

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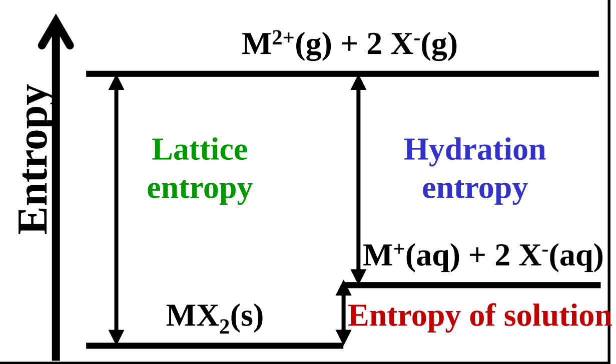
**Free enthalpy of solution = enthalpy of solution – T*entropy of solution**

**i.e. $\Delta G^0_L = \Delta H^0_L - T^*\Delta S^0_L$**



# 2.5 Alkaline Earth Metal Salts

## Solubility of Alkaline Earth Metal Salts in Water

**High Solubility**

Free enthalpy of solution $\Delta G^0_L = \Delta H^0_L - T*\Delta S^0_L < 0$

$\Rightarrow$ $\Delta H^0 < 0$

$\Rightarrow$ $T\Delta S^0 > 0$

**Poor solubility**

Free enthalpy of solution $\Delta G^0_L = \Delta H^0_L - T*\Delta S^0_L > 0$

$\Rightarrow$ $\Delta H^0 > 0$

$\Rightarrow$ $T\Delta S^0 < 0$

**Example $MgCl_2$**

| Lattice enthalpy [kJ/mol] | Hydration enthalpy [kJ/mol] | Enthalpy of solution [kJ/mol] |
|---|---|---|
| -2523 | -2677 | -154 |
| Lattice entropy [J/Kmol] | Hydration entropy [J/Kmol] | Entropy of solution [J/Kmol] |
| 360 | -475 | -115 |

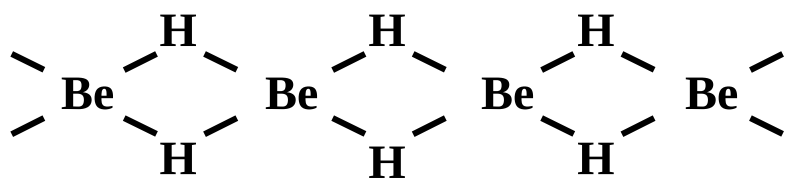
Free enthalpy of solution $\Delta G^0_L$ = -154 kJ/mol – 298 K*(-115 J/Kmol) = - 120 kJ/mol
(at room temperature = 298 K)

# 2.6 Be-Compounds

**Compounds of Beryllium are Similar to Those of Boron in the Sense That They are Characterised by a Shortage of Electrons, Both Form Covalent Bonds and are Highly Toxic**

**<u>Compounds with hydrogen</u>**

- **Polymers $(BeH_2)_n$-chains**




**<u>Compounds with halides</u>**

- **$BeF_2$ is isoelectronic to $SiO_2$ and isotypic to α-quartz and ß-cristobalite, respectively**
- **$BeF_2$ is soluble in $H_2O$ and forms fluoro beryllates together with fluorides: $[BeF_3]^-$, $[BeF_4]^{2-}$, $[Be_2F_7]^{3-}$**
- **$BeCl_2$ exists as a $(BeCl_2)_n$ polymer and is isoelectronic to fibrous $SiO_2$, upon heating, first the dimers Cl=Be(µ-Cl)$_2$Be=Cl, and then the monomer Cl=Be=Cl are formed**

**<u>Compounds with oxygen</u>**

- **$Be(OH)_2$ is amphoteric: $[Be(H_2O)_4]^{2+} \overset{OH^-}{\rightleftharpoons} Be(OH)_2 \overset{OH^-}{\rightleftharpoons} [Be(OH)_4]^{2-}$**
- **BeO exists in a wurtzite-type of structure and is extremely hard $\Rightarrow$ high temperature ceramics**

# 2.7 Mg-Compounds

**Most Magnesium Salts are Hygroscopic and are Thus Often Used as Desiccants ($MgCl_2$, $MgSO_4$)**

**Compounds with hydrogen**

$Mg(s) + H_2(g) \rightarrow MgH_2(s)$

$MgH_2(s) + 2\,H_2O(l) \rightarrow Mg(OH)_2(s) + 2\,H_2(g)$

ionic with rutile-like structure

**Compounds with halides**

$MgF_2$ as AR coatings of optical glasses (low refractive index $n_D = 1.38$)

$MgCl_2$ for the drying of gases $\Rightarrow$ forms hexahydrates

**Compounds with oxygen**

$2\,Mg(s) + O_2(g) \rightarrow MgO(s)$ "magnesia" $\Delta H^0_R = -1204$ kJ/mol

$2\,Mg(s) + CO_2(g) \rightarrow MgO(s) + C(s)$ $\Delta H^0_R = -808$ kJ/mol

MgO is used as a neutralisation agent, crucible and oven material as well as a coating for front panels of plasma displays due to its high emission intensity of secondary electrons ($\gamma_{Ne}$)

$MgCl_2(s) + Ca(OH)_2(s) \rightarrow Mg(OH)_2(s) + CaCl_2(s)$

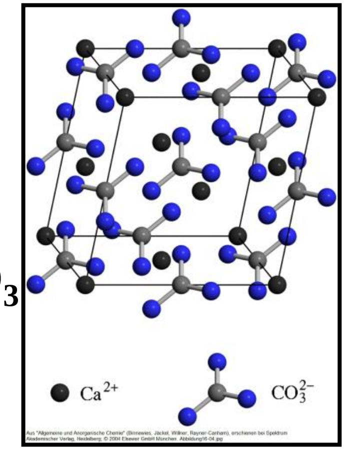
$Mg^{2+}$-solution + $Me_2CO_3 \rightarrow 4\,MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ "magnesia alba"

# 2.8 Ca-Compounds

**Ca-Compounds are of Uttermost Importance as Construction Materials in Nature and Manmade Building Industry**

Lime stone

Structure of calcite




**Compounds with halides**

- $CaF_2$ Flussspat, important in chemistry of fluorine
- $CaCl_2$ desiccant, forms hexahydrates
- By-product during soda production: $CaCO_3 + 2\ NaCl \rightarrow CaCl_2 + Na_2CO_3$

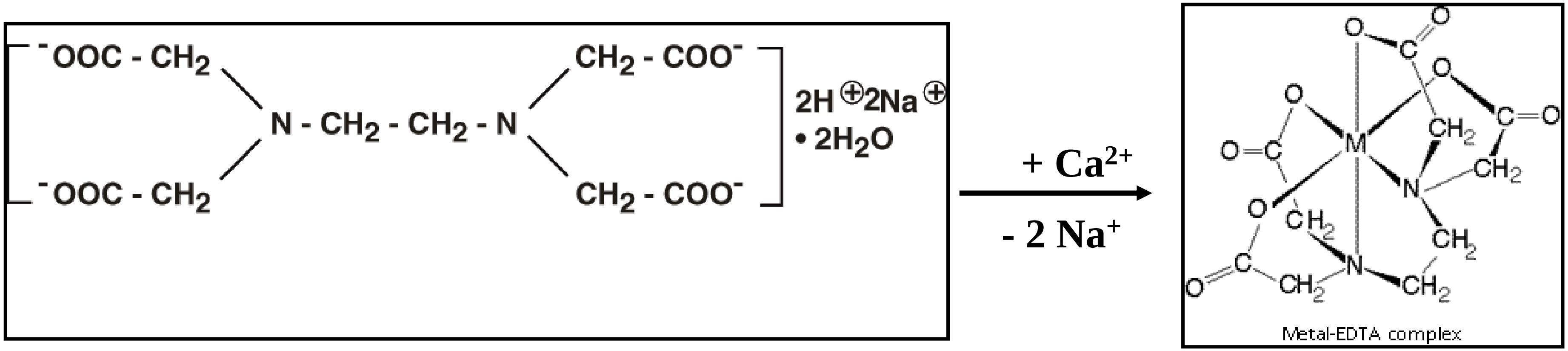
**Compounds with oxygen**

- $Ca + O_2 \rightarrow CaO$ “burnt lime, quicklime“
- $CaO + CO_2 \rightarrow CaCO_3$ “lime“
- $CaO + H_2O \rightarrow Ca(OH)_2$ “hydrated lime“
- $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ “lime mortar“
- $CaCO_3$ as vaterit, aragonite (pearls) and calcite (chalk, limestone, marble)
- Double spar (calcite) as a crystal is birefringent, meaning the refractive index is isotropic which can lead to a duplication of the light beam
- $CaCO_3$ (poorly soluble) + $H_2O + CO_2 \rightarrow Ca(HCO_3)_2$ (readily soluble)

Foraminifers

# 2.8 Ca-Compounds

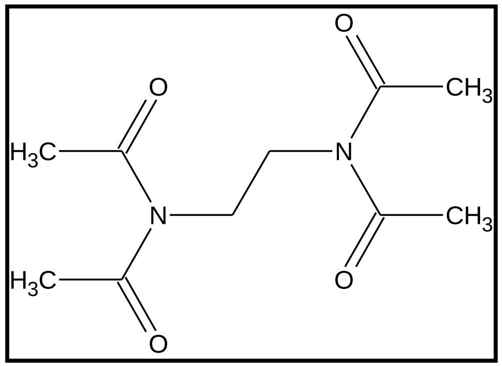
## Calcium and Other Divalent Metal Cations Form Highly Stable Complexes with the Chelating Agent EDTA (Ethylenediaminetetraacetic Acid)




**In order to reduce the hardness of water, EDTA is used as a chelating agent in detergents, where it forms complexes with the $Ca^{2+}$-cations**

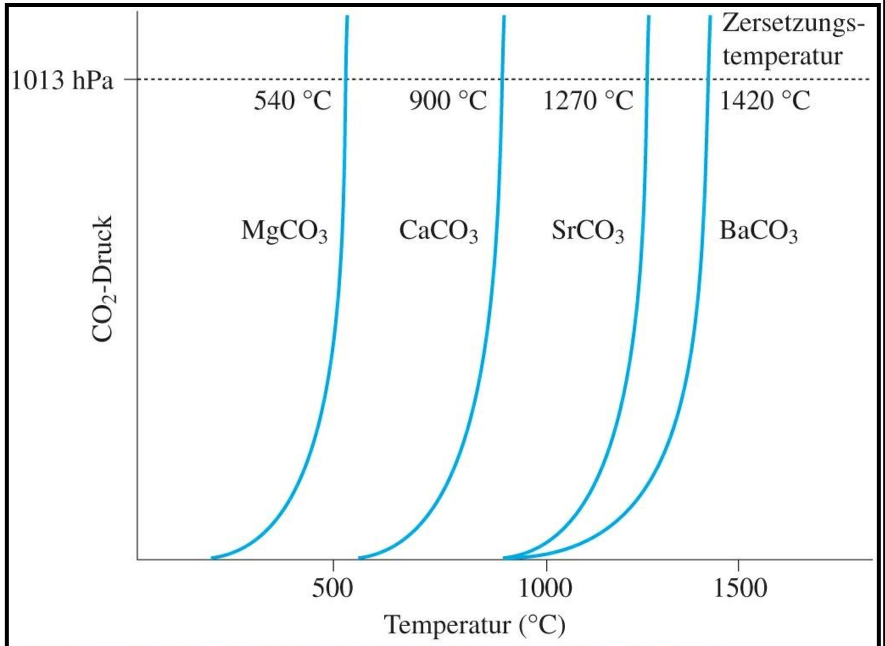
**⇒ The $Ca^{2+}$-cation is coordinated in a octahedral fashion by 4 O- and 2 N-atoms which leads to stericly favourable 5-ring systems**

**TAED (tetraacetylethylenediamine) is used as a bleach activator in detergents**




# 2.9 Ba-Compounds

## Barium Compounds are Important Mainly Due to Their High Density and Their Low Electron Work Function

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**Readily soluble Ba salts**

- $BaX_2$ (X = F, Cl, Br) highly toxic
- $BaCO_3 + 3\ H^+ \rightarrow Ba^{2+} + CO_2\uparrow + H_3O^+$
  $\Rightarrow$ mice and rats poison
- $Ba(NO_3)_2$ as "green fire" $\Rightarrow$ pyrotechnics
- $BaCO_3 \rightarrow CO_2 + BaO$ (material for electrodes)
- $BaO + H_2O \rightarrow Ba(OH)_2$ "barytes water"
- $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

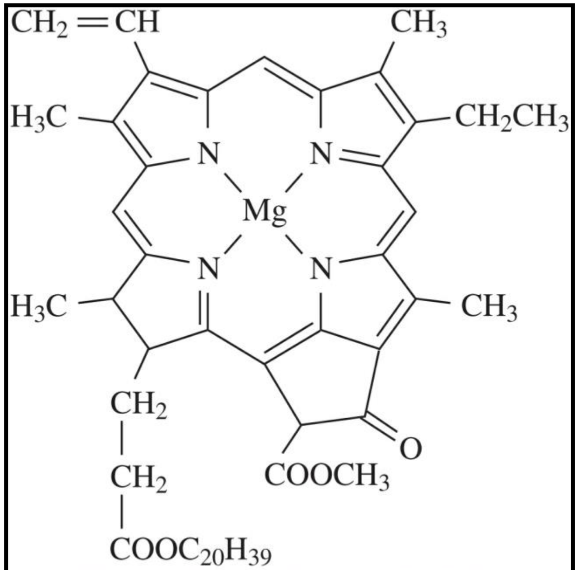
**Poorly soluble Ba salts**

- $BaSO_4$ $\Rightarrow$ contrast agent, white pigment, white standard (spectroscopy)
- $MeSO_4 + C \rightarrow 4\ CO\uparrow + MeS$ (Me = Ca, Sr, Ba)
- These Me-sulphides can be transformed into efficient phosphors by doping with $Eu^{2+}$
  $\Rightarrow$ Application of MgS:Eu (580 nm), CaS:Eu (655 nm) or SrS:Eu (615 nm) as radiation converters in LEDs and EL light sources

# 2.10 Biological Aspects

## Magnesium

- $Mg^{2+}$ is a important ion in bio-inorganic chemistry
  - ⇒ Metal centre in chlorophyll (photosynthesis)
  - ⇒ In the active centres of ATPases and other enzymes
  - ⇒ PCR (Polymerase Chain Reaction)
- Intracellular liquids

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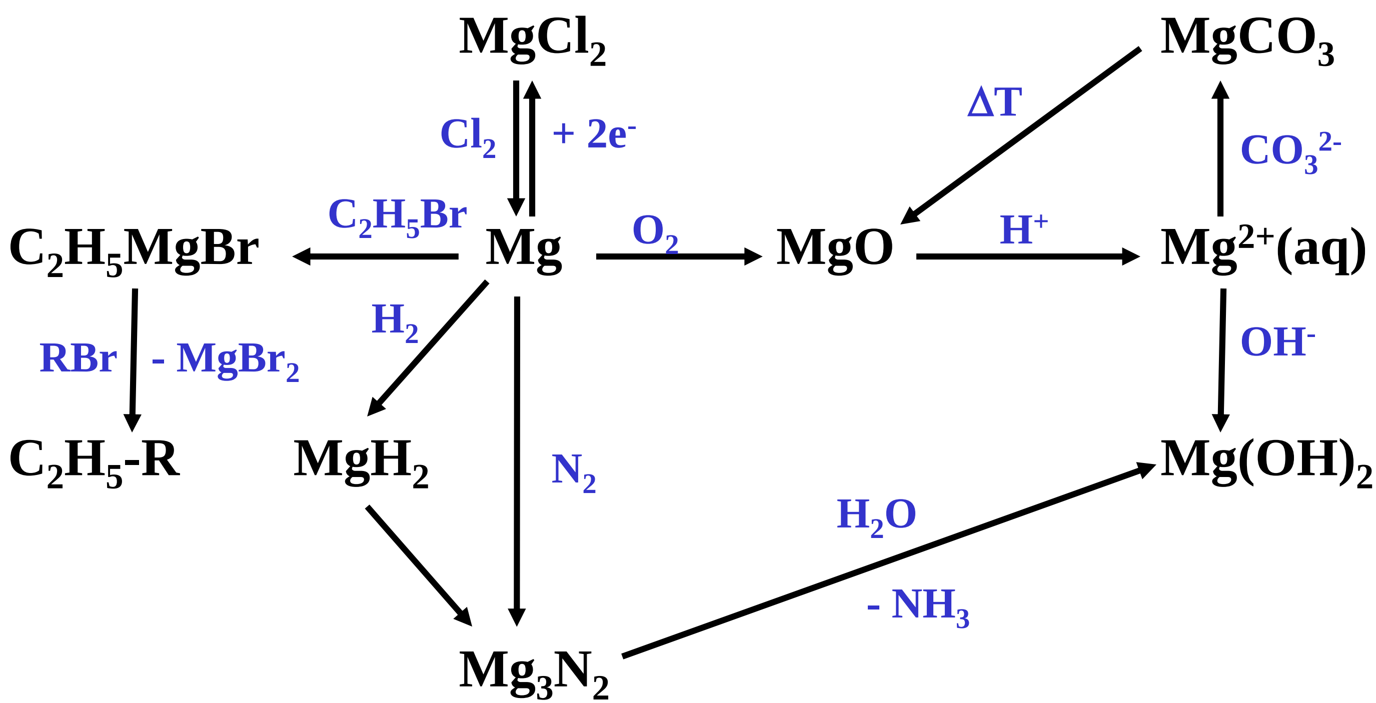
## Calcium

- Extracellular liquids
- Of importance for blood coagulation and muscle contraction
- Exoskeletons: $CaCO_3$
  - Mollusca (mussels, snails)
  - Cnidaria (corals)
- Endoskeletons: $Ca_5(PO_4)_3(OH,X)$ with X = F, Cl → Luminescence by doping with $Mn^{2+}$
  - Chordata and vertebrata
  - Cephalopoda

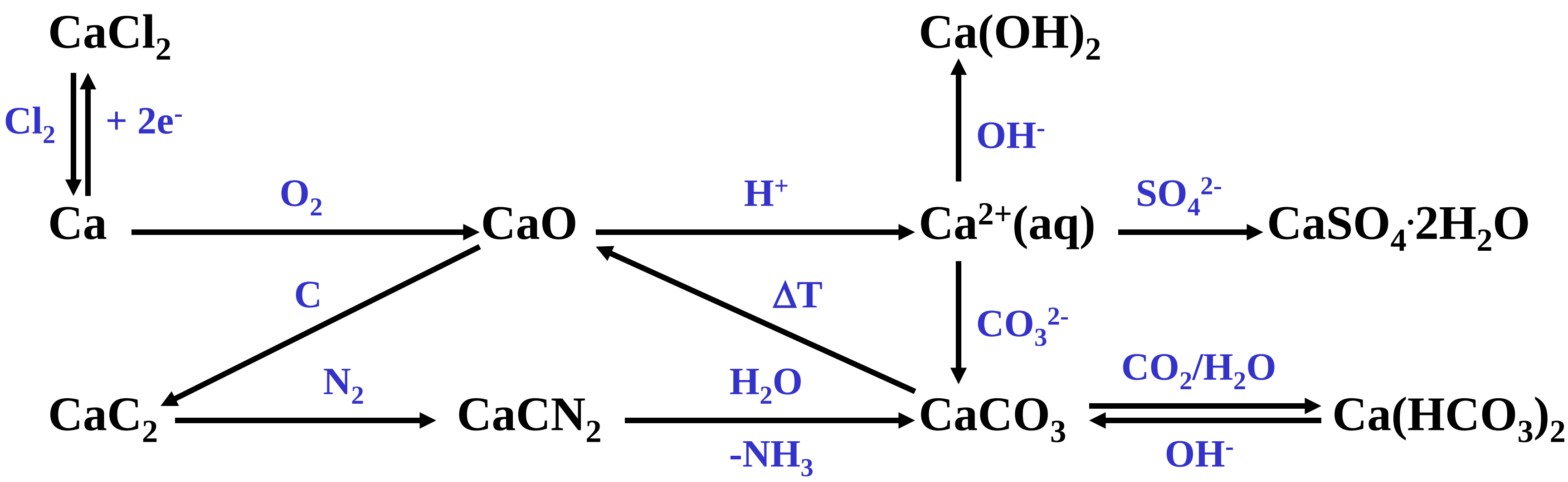
# Overview Magnesium Chemistry

**Oxidation States: 0, +II**



# Overview Calcium Chemistry

**Oxidation Sates: 0, +II**



# Overview Barium Chemistry

**Oxidation States: 0, +II**