# 2. Alkaline Earth Metals

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<table>
<thead>
<tr>
<th>Group</th>
<th>2 or IIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Be</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
</tr>
<tr>
<td>38</td>
<td>Sr</td>
</tr>
<tr>
<td>56</td>
<td>Ba</td>
</tr>
<tr>
<td>88</td>
<td>Ra</td>
</tr>
</tbody>
</table>
## 2.1 Occurrence

### Abundance in the Earth’s Crust

Be: \(2.7 \cdot 10^{-4}\%\), Mg: 1.9\%, Ca 3.4\%, Sr: 3.6\cdot 10^{-2}\%, Ba: 4\cdot 10^{-2}\%

<table>
<thead>
<tr>
<th>Element (Common Name)</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium (beryllos)</td>
<td>(\text{Be}_3\text{Al}_2[\text{Si}<em>6\text{O}</em>{18}])</td>
<td>Beryl, emerald, aquamarine</td>
</tr>
<tr>
<td>greek: Beryl</td>
<td>Al(_2)[BeO(_4)]</td>
<td>Chrysoberyl</td>
</tr>
<tr>
<td></td>
<td>Be(_2\text{SiO}_4)</td>
<td>Phenakite</td>
</tr>
<tr>
<td>Magnesium (magnesia)</td>
<td>(Ca,Mg)CO(_3)</td>
<td>Dolomite</td>
</tr>
<tr>
<td>town in Asia Minor</td>
<td>(Mg,Fe)[SiO(_4)]</td>
<td>Olivine</td>
</tr>
<tr>
<td></td>
<td>Mg(_3)(OH(_2))[Si(<em>4)O(</em>{10})]</td>
<td>Talc</td>
</tr>
<tr>
<td>Calcium (calx)</td>
<td>CaSO(_4)</td>
<td>Gypsum</td>
</tr>
<tr>
<td>latin: lime</td>
<td>CaCO(_3)</td>
<td>Calcite, aragonite</td>
</tr>
<tr>
<td></td>
<td>CaF(_2)</td>
<td>Fluorite</td>
</tr>
<tr>
<td></td>
<td>Ca(_5)(PO(_4))(_3)(OH,F)</td>
<td>Apatite</td>
</tr>
<tr>
<td>Strontium (strontian)</td>
<td>SrSO(_4)</td>
<td>Cölestine</td>
</tr>
<tr>
<td>Place in Scotland</td>
<td>SrCO(_3)</td>
<td>Strontianite</td>
</tr>
<tr>
<td>Barium (barys)</td>
<td>BaSO(_4)</td>
<td>Barite</td>
</tr>
<tr>
<td>greek: heavy</td>
<td>BaCO(_3)</td>
<td>Witherite</td>
</tr>
</tbody>
</table>
### 2.2 Properties

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

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

- 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$_3$N$_2$, 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**
Through reduction of BeF₂ with Mg in graphite crucibles at 1300 °C
BeF₂ + Mg → Be + MgF₂

**Magnesium**
By fused-salt electrolysis of MgCl₂ at 700 – 800 °C
MgCl₂(l) → Mg(s) + Cl₂(g)
Anhydrous MgCl₂(s) can be obtained through MgO(s) + Cl₂(g) + C(s) → MgCl₂(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) → Al₂O₃(s) + 3 Ba(g)
3 BaO(s) + Si(s) → BaSiO₃(s) + 2 Ba(g)
BaO is obtained by thermal decomposition of BaCO₃ → BaO + CO₂↑
2.4 Applications

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

Magnesium
- Density = 1.74 g/cm³ $\rightarrow$ Mg-alloys as light metals in the aviation and automotive industry
- Energy source of the future?: $2 \text{Mg(s)} + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{MgO(s)} \quad \Delta H^0_R = -1204 \text{ kJ/mol}$

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:
  $\text{BaO} + \text{W} \rightarrow \text{Ba}_3\text{WO}_6 + 3 \text{Ba}$ (good thermal e⁻-emitter)
- BaO is used as an additive in glasses to increase the cross-section for x-rays
- CaO shows white $\Rightarrow$ thermo-luminescence “limelight”
The Covalent Character of the Salts and Their Solubility Depends Strongly on the Ionic Charge Density (ICD) of the Cations

<table>
<thead>
<tr>
<th>Ion</th>
<th>CN</th>
<th>Radius [pm]</th>
<th>ICD [C/mm³]</th>
<th>Covalent character of the salts</th>
<th>Solubility of the hydroxides</th>
<th>Solubility of the sulphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be²⁺</td>
<td>4</td>
<td>41</td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>59</td>
<td>370</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4</td>
<td>71</td>
<td>210</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>86</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>6</td>
<td>114</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>126</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>6</td>
<td>132</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>140</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>6</td>
<td>149</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>156</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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(H₂O)₄]²⁺ and (BeCl₂)ₙ
### 2.5 Alkaline Earth Metal Salts

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

<table>
<thead>
<tr>
<th>Ion</th>
<th>Chloride</th>
<th>Nitrate</th>
<th>Sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>MgCl$_2$·6H$_2$O</td>
<td>Mg(NO$_3$)$_2$·6H$_2$O</td>
<td>MgSO$_4$·7H$_2$O</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>CaCl$_2$·6H$_2$O</td>
<td>Ca(NO$_3$)$_2$·4H$_2$O</td>
<td>CaSO$_4$·2H$_2$O</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>SrCl$_2$·6H$_2$O</td>
<td>Sr(NO$_3$)$_2$·4H$_2$O</td>
<td>SrSO$_4$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>BaCl$_2$·2H$_2$O</td>
<td>Ba(NO$_3$)$_2$</td>
<td>BaSO$_4$</td>
</tr>
</tbody>
</table>

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

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

**Free enthalpy of solution** = enthalpy of solution – $T \times$ entropy of solution

\[ \Delta G^0_L = \Delta H^0_L - T \times \Delta S^0_L \]
## 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 MgCl₂**

<table>
<thead>
<tr>
<th>Lattice enthalpy [kJ/mol]</th>
<th>Hydration enthalpy [kJ/mol]</th>
<th>Enthalpy of solution [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2523</td>
<td>-2677</td>
<td>-154</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>-475</td>
<td>-115</td>
</tr>
</tbody>
</table>

Free enthalpy of solution \( \Delta G^0_L = -154 \text{ kJ/mol} - 298 \text{ K} 	imes (-115 \text{ J/Kmol}) = -120 \text{ kJ/mol} \)

(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

Compounds with hydrogen
- Polymers (BeH₂)_n-chains

Compounds with halides
- BeF₂ is isoelectronic to SiO₂ and isotypic to α-quartz and β-cristobalite, respectively
- BeF₂ is soluble in H₂O and forms fluoro beryllates together with fluorides: [BeF₃]⁻, [BeF₄]²⁻, [Be₂F₇]³⁻
- BeCl₂ exists as a (BeCl₂)_n polymer and is isoelectronic to fibrous SiO₂, upon heating, first the dimers Cl=Be(µ-Cl)₂Be=Cl, and then the monomer Cl=Be=Cl are formed

Compounds with oxygen
- Be(OH)₂ is amphoteric: [Be(H₂O)₄]²⁺ ⇌ Be(OH)₂ ⇌ [Be(OH)₄]²⁻
- BeO exists in a wurtzite-type of structure and is extremely hard ⇒ high temperature ceramics
2.7 Mg-Compounds

Most Magnesium Salts Are Hygroscopic and Are Thus Often Used as Desiccants (MgCl₂, MgSO₄)

Compounds with hydrogen
Mg(s) + H₂(g) → MgH₂(s)
MgH₂(s) + 2 H₂O(l) → Mg(OH)₂(s) + 2 H₂(g)
ionic with rutile-like structure

Compounds with halides
MgF₂ as AR coatings of optical glasses (low refractive index n_D = 1.38)
MgCl₂ for the drying of gases ⇒ forms hexahydrates

Compounds with oxygen
2 Mg(s) + O₂(g) → MgO(s) “magnesia“ \(\Delta H^0_R = -1204 \text{ kJ/mol}\)
2 Mg(s) + CO₂(g) → MgO(s) + C(s) \(\Delta H^0_R = -808 \text{ kJ/mol}\)
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
MgCl₂(s) + Ca(OH)₂(s) → Mg(OH)₂(s) + CaCl₂(s)
Mg²⁺-solution + Me₂CO₃ → 4 MgCO₃·Mg(OH)₂·4H₂O “magnesia alba“
2.8 Ca-Compounds

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

Compounds with halides
- CaF₂ Flussspat, important in chemistry of fluorine
- CaCl₂ desiccant, forms hexahydrates
- By-product during soda production: \( \text{CaCO}_3 + 2 \text{NaCl} \rightarrow \text{CaCl}_2 + \text{Na}_2\text{CO}_3 \)

Compounds with oxygen
- \( \text{Ca} + \text{O}_2 \rightarrow \text{CaO} \) “burnt lime, quicklime“
- \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \) “lime“
- \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \) “hydrated lime“
- \( \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \) “lime mortar“
- \( \text{CaCO}_3 \) 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
- \( \text{CaCO}_3 \) (poorly soluble) + \( \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca(HCO}_3)_2 \) (readily soluble)
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 $\text{Ca}^{2+}$-cations

$\Rightarrow$ The $\text{Ca}^{2+}$-cation is coordinated in an octahedral fashion by 4 O- and 2 N-atoms which leads to sterically 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

**Readily soluble Ba salts**
- \( \text{BaX}_2 \) (\( X = \text{F, Cl, Br} \)) highly toxic
- \( \text{BaCO}_3 + 3 \text{H}^+ \rightarrow \text{Ba}^{2+} + \text{CO}_2 \uparrow + \text{H}_3\text{O}^+ \)  
  \( \Rightarrow \) mice and rats poison
- \( \text{Ba(NO}_3)_2 \) as “green fire”  \( \Rightarrow \) pyrotechnics
- \( \text{BaCO}_3 \rightarrow \text{CO}_2 + \text{BaO} \) (material for electrodes)
- \( \text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 \) “barytes water“
- \( \text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O} \)

**Poorly soluble Ba salts**
- \( \text{BaSO}_4 \)  \( \Rightarrow \) contrast agent, white pigment, white standard (spectroscopy)
- \( \text{MeSO}_4 + \text{C} \rightarrow 4 \text{CO} \uparrow + \text{MeS} \) (\( \text{Me} = \text{Ca, Sr, Ba} \))
- These Me-sulphides can be transformed into efficient phosphors by doping with \( \text{Eu}^{2+} \)  
  \( \Rightarrow \) Application of \( \text{MgS:Eu, CaS:Eu, or SrS:Eu} \) as radiation converters
2.10 Biological Aspects

**Magnesium**
- \( \text{Mg}^{2+} \) is an 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

**Calcium**
- Extracellular liquids
- Of importance for blood coagulation and muscle contraction
- Exoskeletons: \( \text{CaCO}_3 \)
  - Mollusca (mussels, snails)
  - Cnidaria (corals)
- Endoskeletons: \( \text{Ca}_5(\text{PO}_4)_3(\text{OH},X) \) with \( X = \text{F}, \text{Cl} \)
  - Chordata and vertebrata
  - Cephalopoda

„Luminescence through doping“
Overview Magnesium Chemistry

Oxidation States: 0, +II

MgCl₂

C₂H₅MgBr

C₂H₅Br

Mg

Cl₂ + 2e⁻

O₂

MgO

H⁺

Mg₂⁺(aq)

ΔT

CO₃²⁻

MgCO₃

OH⁻

Mg(OH)₂

RBr - MgBr₂

H₂

N₂

MgH₂

C₂H₅-R

Mg₃N₂

H₂O

- NH₃

Inorganic Chemistry I
Prof. Dr. T. Jüstel
Overview Calcium Chemistry

Oxidation States: 0, +II

CaCl₂ → Cl₂ + 2e⁻
Ca³⁺(aq) → Ca²⁺(aq) + e⁻
Ca²⁺(aq) + 2OH⁻ → Ca(OH)₂
Ca(OH)₂ → Ca²⁺(aq) + 2OH⁻
Ca²⁺(aq) + SO₄²⁻ → CaSO₄·2H₂O

CaC₂ → C + N₂
CaC₂ → CaCN₂
CaCN₂ → CaCO₃
CaCO₃ → Ca(HCO₃)₂
Overview Barium Chemistry

Oxidation States: 0, +II

\[
\begin{align*}
\text{BaCl}_2 & \quad \text{Cl}_2 & + & 2\text{e}^- \\
\text{Ba} & \quad \text{BaO}_2 & \quad \Delta T & \quad \text{O}_2 \\
\text{BaO} & \quad \text{H}_2\text{O} & \quad -\text{H}_2 \\
\text{Ba(OH)}_2 & \quad \Delta T & \quad \text{CO}_2 & \quad \text{BaCO}_3 & \quad \text{H}_2\text{SO}_4 & \quad \text{BaSO}_4 \\
\text{Ba} & \quad \text{BaO} & \quad \text{H}^+ & \quad \text{Ba}^{2+}(aq) & \quad \text{SO}_4^{2-} & \quad \text{BaS} & \quad \text{C} \\
\end{align*}
\]