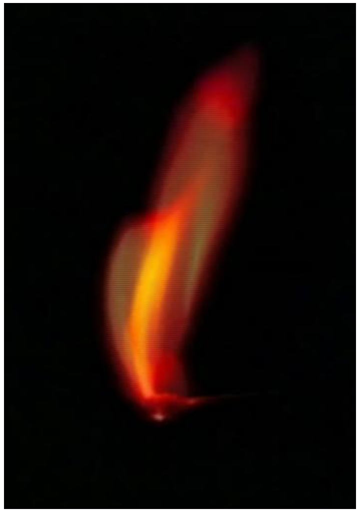
The Alkaline Earth Metals

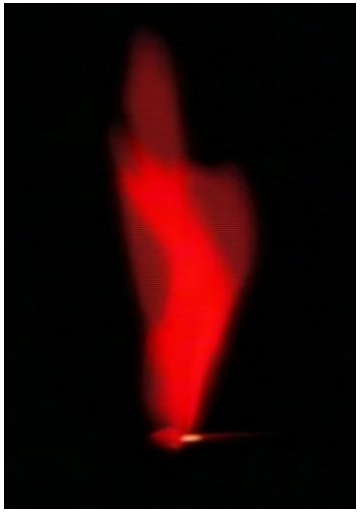
- Isolated by Sir Humphry Davy (Ba, Mg, Ca, Sr) by electrolysis of salts (~ 1808).
- Higher Mp, harder and more dense than the Group I metals.
- Less reactive than Group I metals but they do react with many electronegative elements.
- In compounds **exclusively oxidation state +2**.
- **Be can form covalent bonds** (e.g. $BeCl_2$) but the others form mostly ionic compounds.
- Due to their high reactivity, they do not occur in elemental form in nature.

Element	Symbol	Atomic number	Electronic configuration
Beryllium	Be	4	$[He]2s^2$
Magnesium	Mg	12	$[Ne]3s^2$
Calcium	Ca	20	$[Ar]4s^2$
Strontium	Sr	38	$[Kr]5s^2$
Barium	Ba	56	$[Xe]6s^2$
Radium	Ra	88	$[Rn]7s^2$

Flame Tests



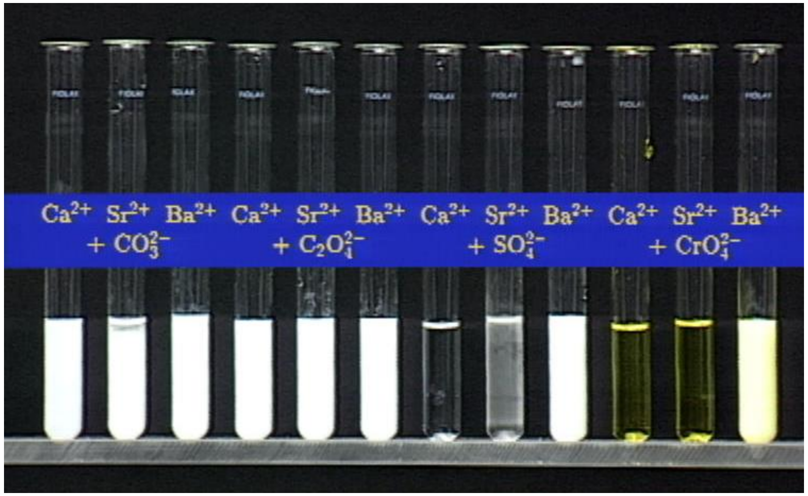
Calcium
orange-red

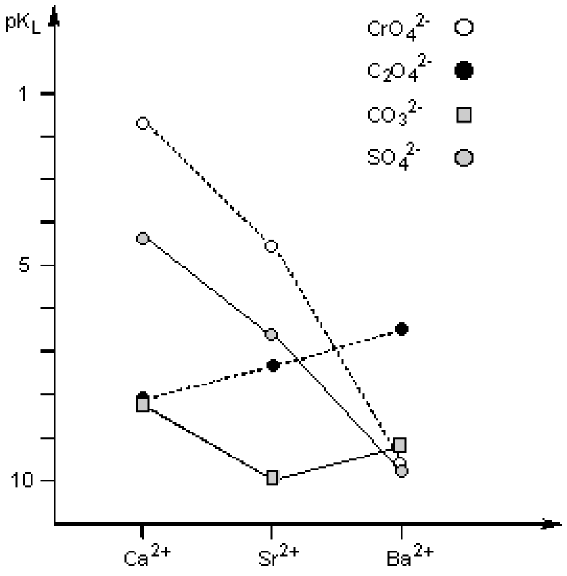


Strontium
carmine-red

Barium
yellow-green

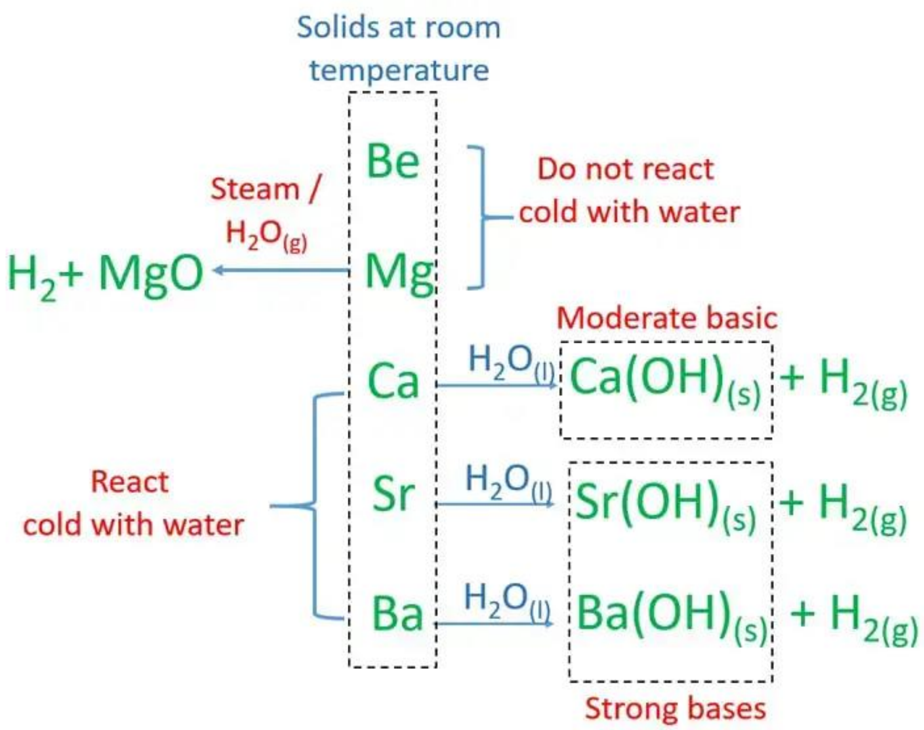
Solubility of Earth Alkaline Salts





- Salts of the singly charged anions are usually soluble.
- Salts of the multiply charged anions are usually insoluble because of the high lattice energy of $M^{2+}X^{2-}$ salts.
- Size matching plays a role: sulphates of the smaller cations Mg^{2+} and Ca^{2+} are soluble while those of the larger cations Sr^{2+} and Ba^{2+} are insoluble.
- We find solubility minima for strontium (carbonates) and calcium (oxalates). This variable behavior demonstrates the fact that the solubility of salt-like compounds is dependent on factors other than just the radius of the ions involved.

Earth Alkaline Metals and Water



Ca, Sr, and Ba react with water but not Be and Mg.

Beryllium

- Beryllium is found in some 30 mineral species, for example beryl (an aluminosilicate). Depending on impurities incorporated into the crystals, the mineral beryl forms a variety of gemstones such as emeralds and aquamarines. Pure beryl is colorless, and additions of chromium can turn the stone green .

- Because beryllium is relatively transparent to X-rays. It is used in X-ray windows

- Beryllium is used as an alloying agent in producing beryllium copper (Cu with 6-7 % Be), which is hard as steel but which has the thermal and electric conductivity of Cu. It is applied as a structural material for high-speed aircrafts, missiles, spacecrafts, and communication satellites.

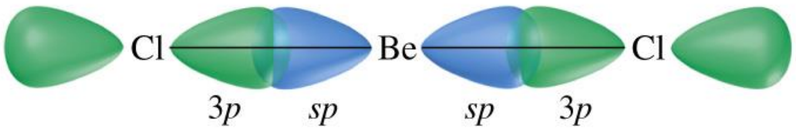
- Be is highly toxic: inhaling dust or fumes that contain beryllium causes inflammation of the lung ('*Berylliosis*').

Green Beryl

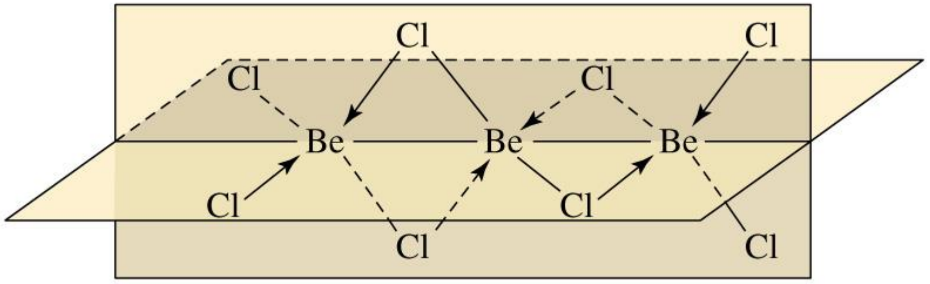
Beryllium copper block

Beryllium Compounds

- Beryllium forms bonds with covalent character.
- $BeCl_2$ forms linear Cl-Be-Cl units in the gas phase and is a poor conductor in the melt (ions are not formed). $BeCl_2$ is electron deficient and thus forms chains in the solid state.



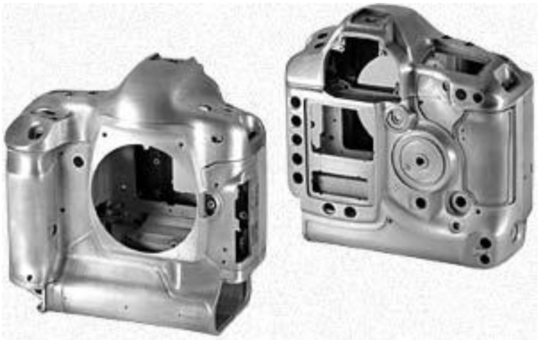
$BeCl_2(g)$
(a)



$BeCl_2(s)$
(b)

Magnesium

- Magnesium is the eighth most abundant element in the earth's crust. It does not occur uncombined but is found in large deposits in the form of magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), and other minerals.
- Sea water contains 0.15 % Mg^{2+}.
- Magnesium is a light, silvery-white, and fairly tough metal. It tarnishes slightly in air, and finely divided magnesium readily ignites upon heating in air and burns with a dazzling white flame.
- It is one-third lighter than aluminum and alloys with Al are essential for airplane and missile construction. The metal improves the mechanical, characteristics of aluminum.
- 80 % of the world's production is obtained by electrolysis of $MgCl_2$.



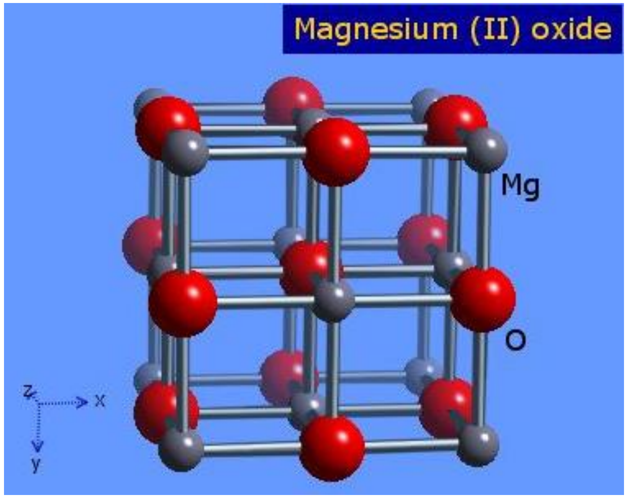
Body made out of Mg alloy.

Magnesia (MgO)

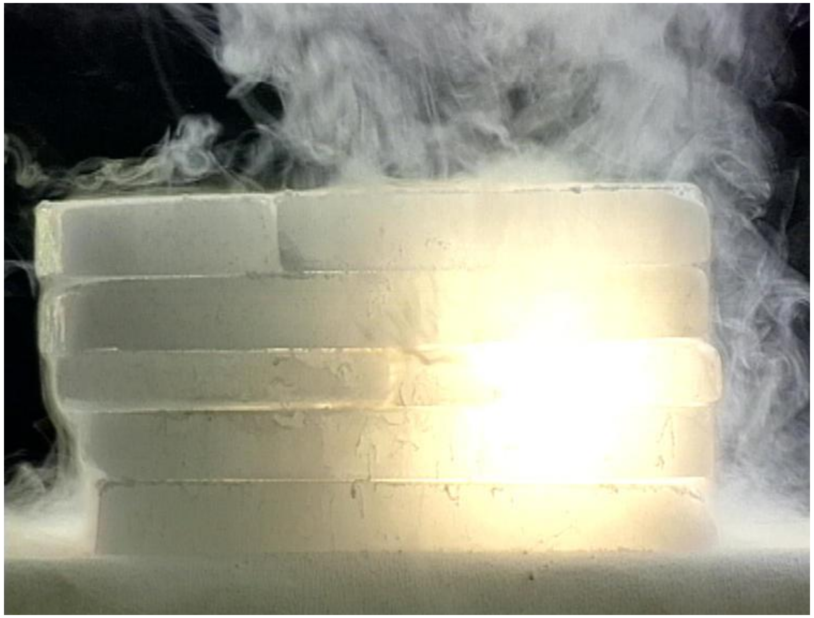
- High Mp (2830 °C), high thermal conductivity and electrical insulator.
- Synthesis: thermal decomposition of $MgCO_3$. The reaction at 800 – 900 °C produces caustic magnesia. Upon heating to 1700 – 2000 °C a highly fire resistant material is obtained, which is used to cover furnaces or heating elements.
- Caustic magnesia hydrates slowly to form sparingly soluble $Mg(OH)_2$ (‘Milk of Magnesia’) – a useful antacid.

$$MgCO_3 \xrightarrow{900\ °C} MgO + CO_2 \xrightarrow{H_2O} Mg(OH)_2$$

$$MgCO_3 \xrightarrow{2000\ °C} \boxed{MgO + CO_2} \not\xrightarrow{H_2O}$$



Reaction of Magnesium with CO_2

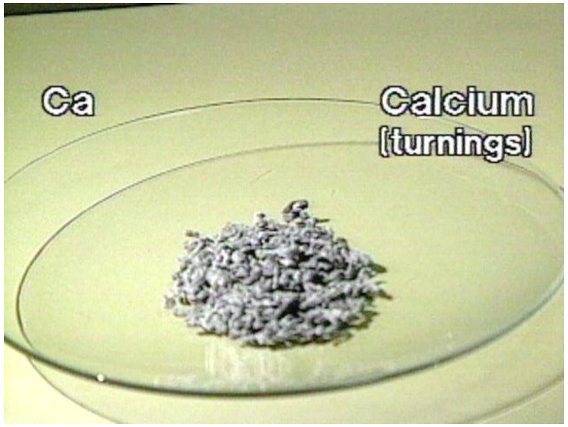


A hole is drilled into the centre of a block of dry ice and filled with strips of magnesium. The metal is lit with a Bunsen burner. As soon as the metal is burning and producing a blinding white light, it is covered with another block of dry ice. As the reaction progresses, the entire block begins to glow. Once the reaction is complete, you will find the black carbon product in the centre of the block.

$$CO_2 + 2\,Mg \longrightarrow 2\,MgO + C$$

Calcium

- Calcium is the fifth most abundant element in the earth's crust.
- The most abundant metal in the human body (~ 1.2 kg in an average adult – most of it in the bones)
- Due to its high reactivity with common materials, there is very little demand for metallic calcium. It is used to remove oxygen, sulfur and carbon from certain alloys.

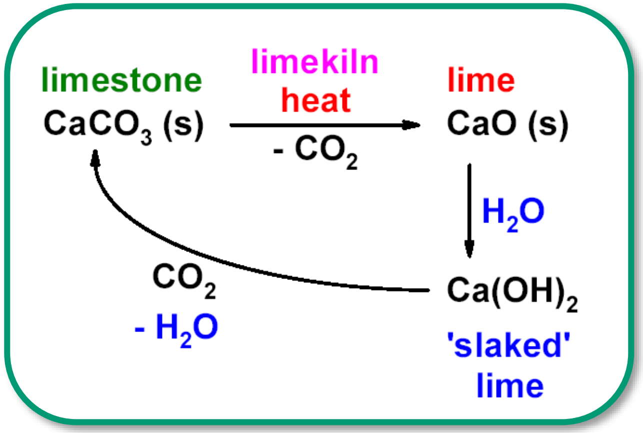


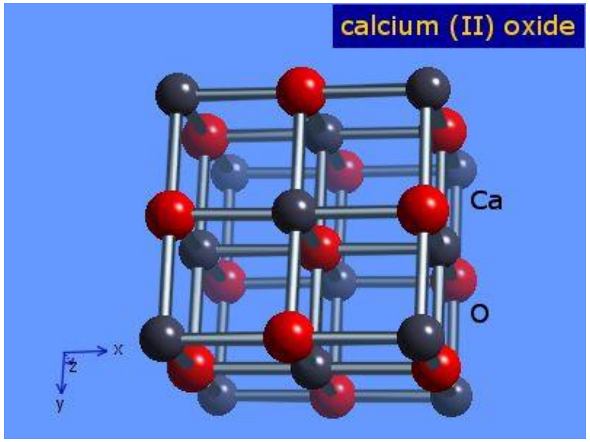
Calcium Chloride ($CaCl_2$)

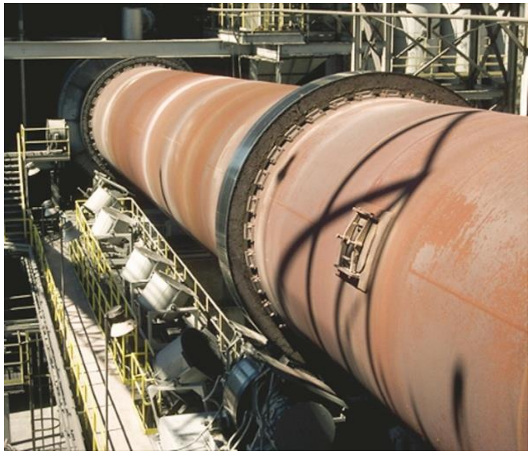
- Crystallizes out of solution as the hexahydrate $[Ca(OH_2)_6]Cl_2$. Contrary to $[Mg(OH_2)_6]Cl_2$ it can be de-hydrated to $CaCl_2$.
- Dissolving $[Ca(OH_2)_6]Cl_2$ is an endothermic process ($\Delta H°$ = positive) → can be used to cool solutions. With ice and $[Ca(OH_2)_6]Cl_2$ it is possible to cool down to – 55 °C.
- Dissolving $CaCl_2$ is an exothermic process ($\Delta H°$ = negative) → can be used to melt ice.

Lime (CaO)

- Obtained by thermal decomposition of limestone (‘limekiln’).
- ‘Slaked lime’ is used in agriculture to adjust the pH of the soil.
- Production of acetylene (see later).
- Formerly used as lighting in theaters. CaO is thermoluminescent (hence the term ‘limelight’).







The decomposition of limestone is carried out in a long rotary kiln

Calcium Carbonate ($CaCO_3$)

- Great historical and current importance as a building material.
- Found all over the world in three forms: chalk, limestone and marble. All three consist of the $CaCO_3$ modification *calcite* (other modifications: *aragonite* and *vaterite*).
- Sensitive to acid rain.

$$CaCO_3\,(s) + H_2SO_4\,(aq) + H_2O\,(l)$$

$$\rightleftharpoons$$

$$CaSO_4(H_2O)_2 + 2\,CO_2\,(g)$$

gypsum

more soluble 'stone leprosy'

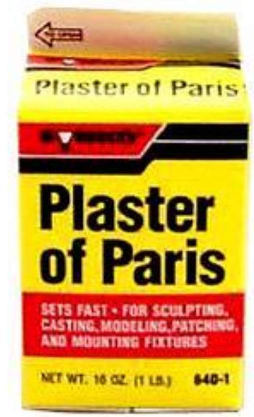
Chalk
'The White Cliffs of Dover'

Limestone

Marble

Gypsum ($CaSO_4$ x 2 H_2O)

- Calcium sulfate is found in nature as gypsum and as $CaSO_4$.
- $CaSO_4$ crystallizes from water as the dihydrate $CaSO_4(H_2O)_2$.
- Dehydration produces the soft hemi-hydrate $CaSO_4(H_2O)_{0.5}$ (‘Plaster of Paris’). Re-hydration forms hard, interlocked gypsum crystals.
- Also commonly used as blackboard ‘chalk’ (rather than real chalk $CaCO_3$).



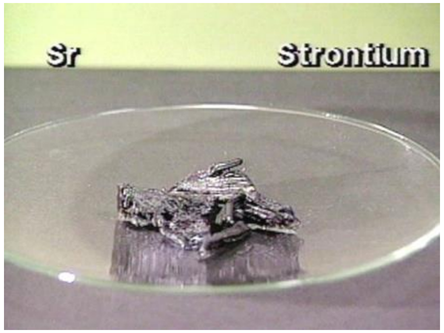
hard		soft

$$\underset{\text{gypsum}}{\overset{\text{hard}}{CaSO_4(H_2O)_2\,(s)}} \xrightarrow{\text{heat}} \underset{\text{Plaster of Paris}}{\overset{\text{soft}}{CaSO_4(H_2O)_{1/2}\,(s)}} + H_2O\,(g)$$

H_2O

Strontium

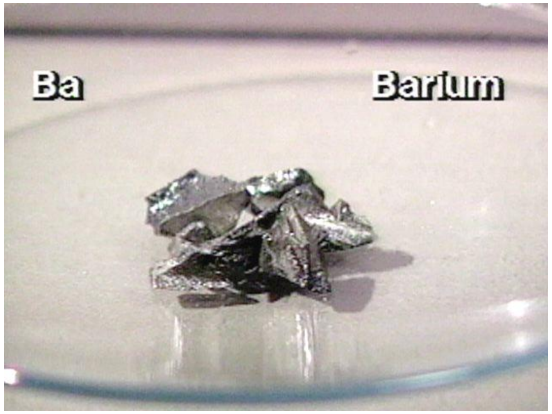
- Strontium is obtained from two of its most common ores, celestite ($SrSO_4$) and strontianite ($SrCO_3$).
- The strontium chloride, usually mixed with potassium chloride (KCl), is melted and electrolyzed, forming strontium and Cl_2.
- Strontium salts → red color in fireworks.
- Strontium-90, a radioactive isotope of strontium, is a common product of nuclear explosions. It is especially deadly since it has a relatively long half-life (28 y) and is absorbed by the body, where it accumulates in the skeletal system.



Celestite

Barium

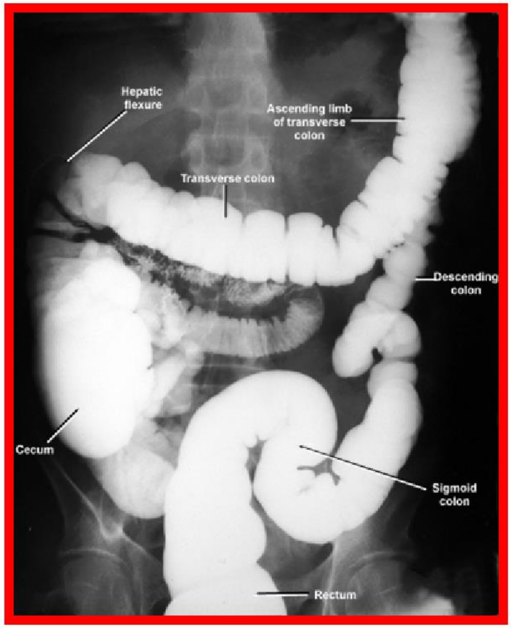
- Barium is most commonly found as the mineral barite ($BaSO_4$) and witherite ($BaCO_3$).
- High purity Ba is produced through the electrolysis of $BaCl_2$.
- Elemental Ba has few industrial applications.
- Its soluble salts are highly toxic.



Barite

Barium Sulfate ($BaSO_4$)

- $BaSO_4$ is the most important natural barium compound.
- Combined with zinc oxide (ZnO) to make a white pigment known as lithophone or with sodium sulfate (Na_2SO_4) to make another white pigment known as blanc fixe.
- The low solubility of $BaSO_4$ makes it useful for the quantitative analysis of SO_4^-.
- Can be used for the X-ray imaging of the colon.
- Although all barium compounds are poisonous, barium sulfate can be safely ingested since it does not dissolve in water.



$BaSO_4$ is a radiopaque agent (it blocks X-rays)

Radium

- Discovered by Pierre and Marie Curie in 1898.
- Powerful α-emitter: burns skin without ‘heat’ and glows on its own by ionizing the surrounding air.
- Rapidly adopted by society for many uses: a) ‘glow in the dark’ paints on watch dials; b) cure for illnesses including anemia and cancer.
- Radiation was later shown to be extremely dangerous: Marie Curie died of leukemia, as did her daughter Irene (also a Nobel prize winner) and many workers that used radium paint.

Marie Curie
(1867 – 1934)
‘Nothing in life is to be feared,
It is only to be understood’

$$^{226}_{88}\mathrm{Ra} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{222}_{86}\mathrm{Rn}$$

Radium and Beauty

http://home.gwi.net/~dnb/gallery/radior/radior.htm

'Radium and Beauty'
New York Tribune
Sunday November 10, 1918.

Luminous Paint

The luminous paint on the hands and numerals of this mid-20th Century alarm clock contain a small quantity of radium bromide mixed with zinc sulfide. The latter converts the energy in the alpha particles emitted by the decaying radium atoms to visible light. For this reason luminous paint containing radium does not need to be "charged up" by exposure to light as do modern clock dials. The half life of radium is 1600 years which means the paint will continue to glow for many centuries. Unfortunately it will also continue to produce dangerous radon gas, which is one of several reasons radium's application in luminous paint has ceased.