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NATURAL STONE

1 - MINERALOGY

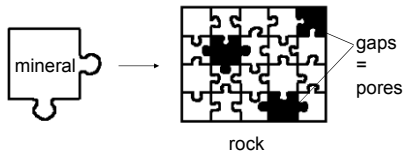
Story materials and conservation of the built heritage - Natural Stone - Mineralogy - BR 1



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Definitions

Natural Stone = Rock = natural material constituting the crust and mantle. Generally, it is solid (≠ unconsolidated sediments like sand) and made of aggregate of **minerals** more or less closely knitted together (gaps = **pores**)



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Definitions

Mineral = **inorganic** natural compound (although some of them may be bioproducts like apatite, calcite, oxalates...) with a **definite chemical composition**, an **atomic structure** and **physical properties** of its own. Generally, it is **solid** (≠ mercury)

Cristal = **homogeneous solid** composed of atoms, ions or molecules with an **organized arrangement** that is **repeated periodically** in three dimensions of space (cristal ≠ amorphous compounds)

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Classification of minerals

According to chemical composition and crystal structure.
Example: Nickel-Strunz Classification - 10th edition
(system adopted by the International Mineralogical Association):

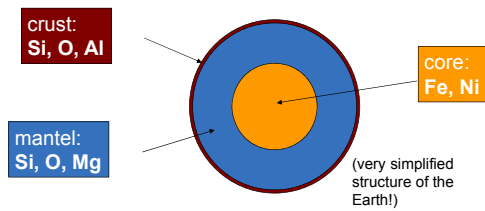
1. **Native elements** (C, S, Au, Ag, Cu, Bi, As, Sb,...)
2. **Sulfides (S^{2-}) and sulfosalts** (selenides, tellurides, ...)
3. **Halides** (Cl^- , F^- ,...)
4. **Oxides (O^{2-}), hydroxides (OH^-)**
5. **Carbonates (CO_3^{2-}), nitrates (NO_3^-)**
6. **Borates** (borax,...)
7. **Sulphates (SO_4^{2-})** (+ thiosulfates, chromates, molybdates,...)
8. **Phosphates (PO_4^{3-})**
9. **Silicates** ($(Si,Al)_xO_{2x} + /-alk. \text{ and } alk. \text{ earth met.}$)
10. **Organic compounds** (formates, oxalates, acetates, hydrocarbons, amber...)

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Distribution of elements within the earth



→ **silicates (& other light minerals) are the most abundant minerals in the earth's surface**

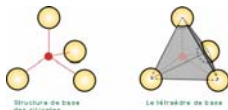
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The silicate class

The silicates are the largest, the most interesting and the most complicated class of minerals. $\approx 30\%$ of all minerals are silicates and 90% of the Earth's crust is made up of silicates.



Le bilan des charges

Oxygène (O^{2-})	: $4 \times 2 = -8$
Silicium (Si^{4+})	: $1 \times 4 = +4$
	excès : -4

The basic chemical unit of silicates is the (SiO_4) tetrahedron shaped anionic group **with a negative four charge (-4)**.
But a mineral must be neutral !!!

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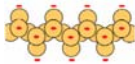


The silicate class - Neutralization of charges...

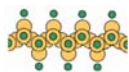
- with cations :



- polymerization with sharing the O^{2-} anions :



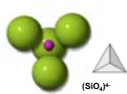
- combining the two previous solutions :





The silicate class - The 6 groups of silicate minerals

Nesosilicates



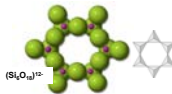
ex.: olivine, garnet, zircon,...

Sorosilicates



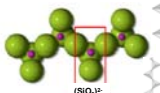
ex.: epidote,...

Cyclosilicates



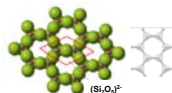
ex.: beryl, tourmaline,...

Inosilicates



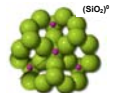
ex.: pyroxene, amphibole,...

Phyllosilicates



ex.: mica, clay,...

Tectosilicates



ex.: quartz, feldspar,...



The silicate class - The clay minerals (phyllosilicates)

Example of 1:1 (or T-O) layer silicate : kaolinite

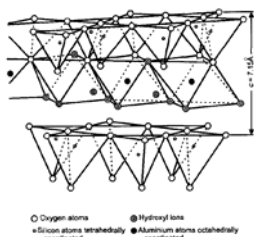


FIG. 1. Kaolinite structure.

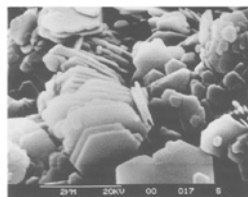


FIG. 2. SEM of kaolinite (Capim River).



The silicate class - The clay minerals (phyllosilicates)

Example of 2:1 (or T-O-T) layer silicate : smectite

= montmorillonite = bentonite

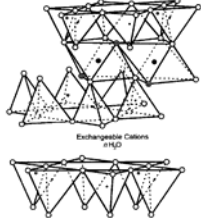


FIG. 4. Smectite structure.

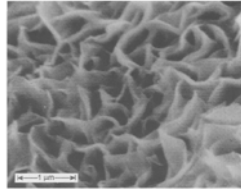


FIG. 5. SEM of Na-montmorillonite (Wyoming).

H. H. Murray, 1999, *Applied clay mineralogy today and tomorrow*, Clay Minerals, V.34, p. 39-49

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The silicate class - The clay minerals (phyllosilicates)

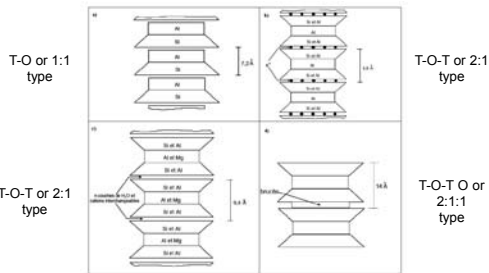


Figure II-9: Schéma de la partiede a) kaolinite, b) illite, c) smectite et d) chlorite

Truche, C., 2010. *Caractérisation et quantification des minéraux argileux dans les sols expansifs par spectroscopie infrarouge aux échelles du laboratoire et du terrain*. Thèse de doctorat, Université Paul Sabatier, Toulouse, 226 p.

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The silicate class - The clay minerals (phyllosilicates)

name	type	particle diameter (µm)	specific surface area (m²/g)	CEC (meq/100g)
Kaolinite	1:1	0.1 - 4	10 - 30	3 - 15
Illite	2:1	0.1 - 1	100 - 175	25 - 40
Smectite (montmorillonite)	2:1	0.1	700 - 840	80 - 100
Vermiculite	2:1	0.1	760	100 - 150
Chlorite	2:1:1	0.1	20	5 - 15

Tableau 6: Caractéristiques des différentes familles d'argile.

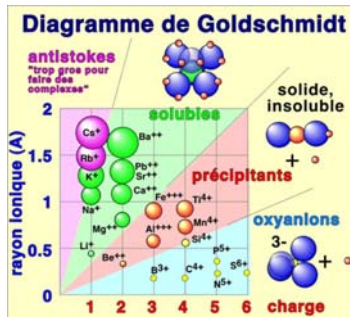
CEC = cation exchange capacity

Truche, C., 2010. *Caractérisation et quantification des minéraux argileux dans les sols expansifs par spectroscopie infrarouge aux échelles du laboratoire et du terrain*. Thèse de doctorat, Université Paul Sabatier, Toulouse, 226 p.

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The silicate class - The clay minerals (phyllosilicates)

Ionic radius
&
cation exchange
capacity



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Additional document on
<http://www.csc-sarl.ch>:
(under the schedule)
Structure of a few silicate minerals

[illegible]

114

Minerals and rocks

Cardinal minerals:

60 to 70% of the rock (usually white or slightly colored)
quartz, feldspars, feldspathoids, calcite

Essential minerals:

20 to 25% of the rock (often dark)
micas, amphiboles, pyroxenes, olivine,...

Accessory minerals:

5 to 10% of the rock
oxides, sulfides,...

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Genesis of minerals and rocks

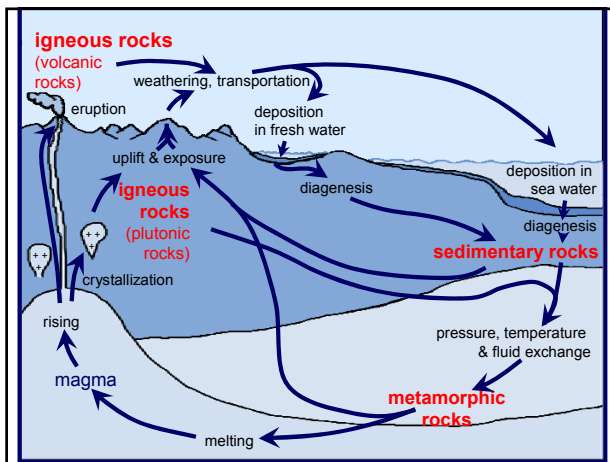
Endogenous genesis (in depth)

- **magmatic process:** coming from a magma
- **metamorphic process:** transformation of pre-existent mineral materials

Exogenic genesis (at the surface)

- **sedimentary process:** pre-existent mineral materials transformation and/or neo-formation

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A few silicate minerals

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Nesosilicates / Garnets $(X_2^{2+}Y_2^{3+}[\text{SiO}_4]_3)$



Use: gemstone, abrasive



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Inosilicates / Amphiboles

Bleu asbestos: Crocidolite $(\text{Na}_2(\text{Fe,Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2)$



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Inosilicates / Amphiboles

Brown asbestos: Amosite $(\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2)$



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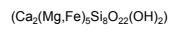


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Inosilicates / Amphiboles

Green asbestos. ex. : Actinolite



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Phyllosilicates / Micas

Muscovite $(\text{KAl}_2[(\text{OH}, \text{F})_2\text{AlSi}_3\text{O}_{10}])$ white mica,

Biotite $(\text{K}(\text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+})_2[(\text{OH}, \text{F})_2\text{Al}(\text{Fe}^{3+}, \text{Ti}^{3+})\text{Si}_3\text{O}_{10}])$ black/brown mica

Use: Heat, acoustic and electric insulator, paints



muscovite



biotite

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Phyllosilicates / Clay minerals

Kaolinite $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$

Use:
porcelain
manufacture,
filler in papers



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Phyllosilicates / Clay minerals

Kaolinite $(Al_2Si_2O_5(OH)_4)$

TABLE 2. Industrial uses of kaolin.

Paper coating	Cement	Food additives
Paper filling	Pencil leads	Bleaching
Extender in paint	Adhesives	Fertilizers
Ceramic raw material	Tanning leather	Plaster
Filler in rubber	Pharmaceuticals	Filter aids
Filler in plastics	Enamels	Cosmetics
Extender in ink	Pastes and glues	Crayons
Cracking catalysts	Insecticide carriers	Detergents
Fibreglass	Medicines	Roofing granules
Foundries	Sizing	Linoleum
Desiccants	Textiles	Polishing compounds

H. H. Murray, 1999. *Applied clay mineralogy today and tomorrow*, Clay Minerals, V.34, p. 39-49

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Phyllosilicates / Clay minerals

Montmorillonite $((Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O)$

Swelling clay mineral exchanger of ions

Use: gastric plaster, cleaner of greases (Terre de Sommières), bentonite, container for the nuclear waste




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Phyllosilicates / Clay minerals

Montmorillonite $((Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O)$

= smectite = bentonite

TABLE 3. Industrial uses of smectites.

Drilling mud	Medical formulations	Crayons
Foundry bond clay	Polishing & cleaning agents	Cement
Pelletizing iron ores	Detergents	Desiccants
Sealants	Aerosols	Cosmetics
Animal feed bonds	Adhesives	Paint
Bleaching clay	Pharmaceuticals	Paper
Industrial oil absorbents	Food additives	Fillers
Agricultural carriers	De-inking of paper	Ceramics
Cat box absorbents	Tape-joining compounds	Catalysts
Beer and wine clarification	Emulsion stabilizer	Pencil leads

H. H. Murray, 1999. *Applied clay mineralogy today and tomorrow*, Clay Minerals, V.34, p. 39-49

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Phyllosilicates / Clay minerals

Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$)

Use of talc:
cosmetic,
lubricant,
manufacture of
paper, excipient
and lubricant in
the
pharmaceutical
industry, tailor's
chalk



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Phyllosilicates / Chlorites

$((\text{Mg}, \text{Fe}, \text{Mn}, \text{Al})_8(\text{Si}, \text{Al})_4\text{O}_{10})(\text{OH})_2$

Use:
decorative stone



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Phyllosilicates / Serpentinities

White asbestos: Chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$)

Use: reinforced cement,
machine parts under
friction, joints for high
temperature machines...
because non flammable,
imputrescible, flexible,
resistant to the majority of
chemicals and with a high
breaking stress => majority
of the world market of
asbestos



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<http://www.ec.gc.ca/nopp/docs/consul/rotterdam/can/fr/chrysotileBG.cfm>

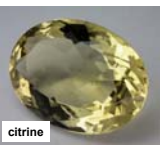
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Tectosilicates / Quartz

(SiO_2)

Use:
Piezoelectric
(clock industry, ...) and...






gemstones (amethyst, citrine)...
cryptocrystalline varieties: flint,
agate, onyx, carnelian,
jasper, opal

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Tectosilicates / Feldspars

K-feldspars (KAISi_3O_8)

Use:
ceramics,
porcelain, glass,
bricks, soaps,
scouring
powders,
gemstones









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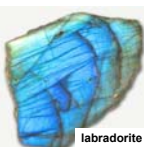
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Tectosilicates / Feldspars

Plagioclases ($\text{AlSi}_3\text{O}_8(\text{Ca,Na})$)

Use:
ceramics,
porcelain, glass,
bricks, soaps,
scouring
powders,
gemstones





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Tectosilicates / Feldspathoids

Lazurite ((Na, Ca)₈(Al, Si)₁₂O₂₄S₂ FeS- CaCO₃)



Use: gemstone, blue pigment

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A few non silicate minerals

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Carbonates / Calcite (CaCO₃)

Use: white pigment (calcite as chalk used since prehistory), raw material of lime



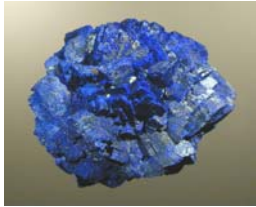
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Carbonates / Azurite ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$)

Use: blue pigment, gemstone



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Carbonates / Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$)

Use: green pigment, gemstone



polished roller



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Carbonates / Cerussite (PbCO_3)

Use: cosmetic (in the past since antiquity); white pigment (= white lead)



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Sulfates / Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)



Selenite (= pierre de lune)



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Sulfates / Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Use: raw material of plaster; fertilizer and soil conditioner, Tofu coagulant, blackboard chalk



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Sulfates / Gypsum alabaster ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Use: decorative stone



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Sulfates / Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Weathering mineral: coming from the air pollution, the stone itself or from cements => degrading stones



granular disintegration



efflorescences



black crust

Study materials and conservation of the built heritage – Natural Stone, Mineralogy, BR 143



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Sulfates / Barite (BaSO_4)

Use: major source of barium, white pigment (blanc fixe), used in paper or paint manufacturing, radiography, heavy filler



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Halides / Halite (NaCl)

Use: table salt, road salt

Danger for building stones: crystallisation damp patches



Study materials and conservation of the built heritage – Natural Stone, Mineralogy, BR 145



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Halides / Sylvite (KCl)

Use: fertilizer, substitute for table salt, lethal injection

Danger for building stones:
crystallisation,
damp patches



Study materials and conservation of the built heritage – Natural Stone, Mineralogy, BR 146



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Halides / Fluorite (CaF₂)

Use:
manufacture of hydrofluoric acid, enamels, glass fibre; used as camera lens; purple pigment; gemstone



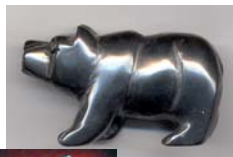
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Oxides / Hematite (Fe₂O₃)

Use: red pigment; gemstone



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Oxides / Goethite ($\text{FeO}(\text{OH})$)

Use: yellow pigment



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Oxides / Rutile (TiO_2)

Use: white pigment (artificial); manufacture of paints; +/- in gemstones



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Oxides / Corundum (Al_2O_3)

Use: abrasive; gemstones



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Oxides / Minium (Pb_3O_4)

Use: red pigment, manufacture of glass, protecting paint against the corrosion of metals



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Oxides / Massicot (or litharge) (PbO)

Use: yellow pigment, manufacture of glass, of oils and varnishes (desiccant), production of insecticides



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Sulfides / Galena (PbS)

Use: black pigment, cosmetic (khol), semiconductor in old wireless systems



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Sulfides / Pyrite (FeS_2) (= fool's gold)

Use: production of sulfur dioxide for paper industry or manufacturing of sulfuric acid

"Dangers" in building oxidation makes it dangerous in aggregates of concrete; rust patches on stones (marble, sandstones,...)



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Sulfides / Realgar (As_2S_3)

Use: red pigment; fireworks

Problems: unstable with light ($\Rightarrow$ yellow pararealgar)



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Sulfides / Orpiment (As_2S_3)

Use: yellow pigment; production of semiconductors and photoconductors, fireworks

Problems: incompatible with pigments like lead and copper-based; it blackens in contact with the air



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Sulfides / Cinnabar (HgS)

Use: red pigment; medicine, drug, food dye

Problems: it blackens in contact with the air



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Phosphates / Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$)

Use: fertilizer; gemstone; new stone consolidant



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Elements / Gold (Au)

Use: noble metal, decorative metal, gilding, conductive coating, money



Study materials and conservation of the built heritage – Natural Stone, Mineralogy, BR 161



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Elements / Silver (Ag)

Use: noble metal;
decorative metal;
printed circuits;
electrical contacts;
dental alloys;
antibacterial;
money



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The identification criteria of minerals

Cleavage / fracture: in some minerals, bonds between layers of atoms aligned in certain directions are weaker than bonds between different layers. In these cases, breakage occurs along smooth, flat surfaces parallel to those zones of weakness



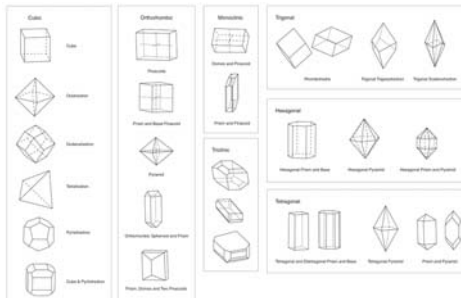
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The identification criteria of minerals

Crystal shape:
the 7 crystal systems



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The identification criteria of minerals

Twinning (macle): Crystal twinning occurs when two separate crystals share some of the same crystal lattice points in a symmetrical manner. The result is an intergrowth of two separate crystals in a variety of specific configurations.



microcline



gypse



orthose



staurotide



pyrite

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The identification criteria of minerals

Density: physical constant (2.7 g/cm³ for silicates)

Colour: not a differential criteria

Streak (trait): colour of the powder, more reliable than the colour of the mineral itself (Scratch unglazed porcelain => This only works for minerals which are softer than a ceramic tile (hardness ~ 7))

Luster (éclat): aspect of the surface mineral when it reflects light

Flam test: the color of flames depends on the chemical composition (Ca: red, Na: yellow, Cu: blue or green, K: violet...)

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The identification criteria of minerals

Hardness: Mohs scale of relative mineral hardness



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The identification criteria of minerals

Reaction with dilute HCl (10%):

carbonates + HCl 10% => emission of CO_2 = effervescence
(calcite (CaCO_3) fizzes readily in either massive or powdered form, but dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) reacts best as a powder or with heated acid)

Touch

Flavour

Smell

Radioactivity

Magnetism,...

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The identification criteria of minerals

Optical properties:



Polarizing microscope

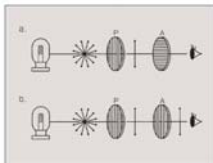


Fig. 1.3 a) crossed nicols and b) parallel nicols
P: polarizer A: analyzer



Interference colors

For more details, see for ex.:

http://www.olympusamerica.com/files/seg_polar_basic_theory.pdf (english)

http://www.kasuku.ch/pdf1.php#a_microscope (french)

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Additional document on <http://www.csc-sarl.ch>:

(under the schedule)

Table of minerals (from Dr Jan-Michael Lange of the Senckenberg Natural History Museum in Dresden, adapted by Dr Christine Bläuer of CSC, Fribourg)



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- <http://www.kasuku.ch/>

English bibliography

- <http://webmineral.com/>

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