CZECH REPUBLIC
DEVELOPMENT COOPERATION

Course and Field-Workshop:

Environmental Geochemistry

Lecturer:

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Arba Minch, Ethiopia, Oct 15 to 23, 2014

How to define … Environmental Geochemistry…

Geochemistry - a science that deals with the chemical composition and chemical changes/reactions in the solid Earth and its various components (***lithosphere***: rocks, minerals, ***hydrosphere:*** oceans, rivers, lakes, and ***atmosphere***: a gaseous shell of our planet)

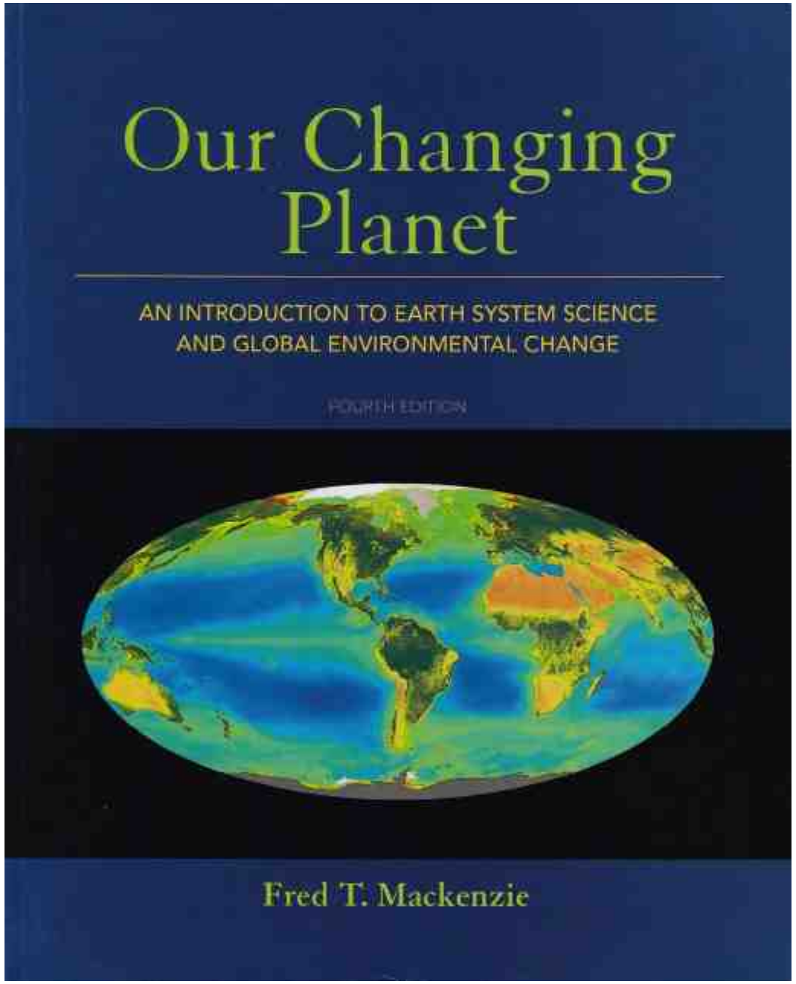
More specifically, it investigates the relative abundance, distribution, and transport of the Earth's chemical elements (e.g., C, O) and their isotopes ($^{13}C/^{12}C$, $^{18}O/^{16}O$).

Environmental Geochemistry:

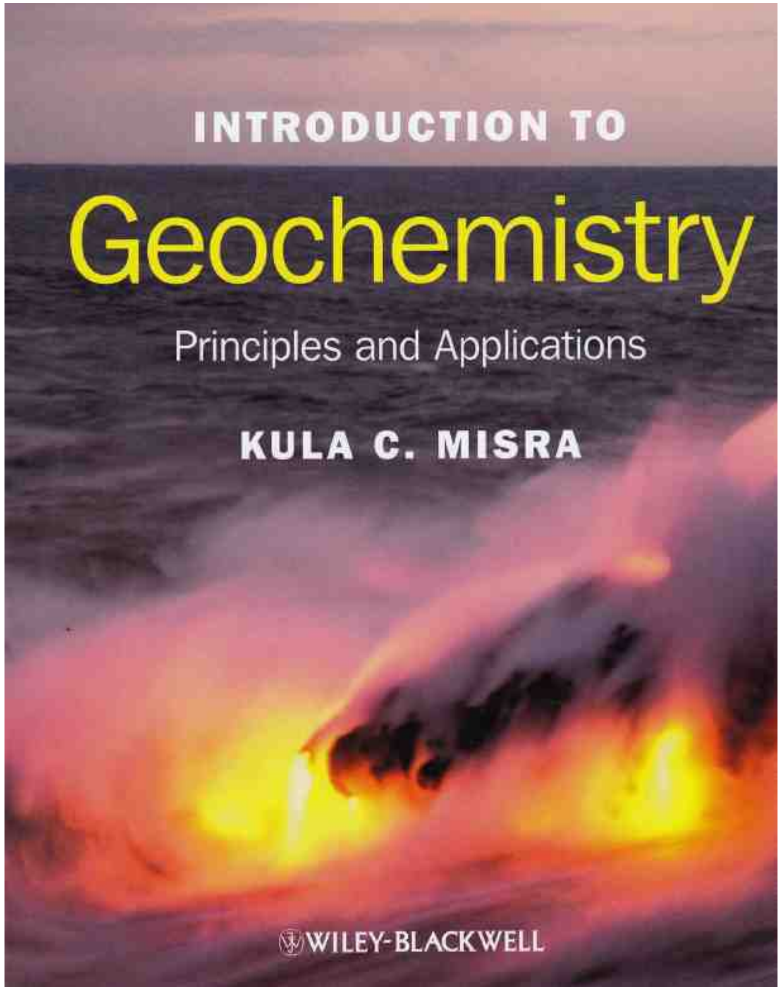
Investigates the impact of natural geochemical processes, and human-induced (anthropogenic) environmental perturbations, on our natural systems (e.g. rivers, lakes, soils, forests) as well as on human health.

Course Textbooks:

By F. T. Mackenzie (Fourth Edition, 2011)



By K.C. Misra, (First Edition, 2012)



Main objectives of this course:

To acquire basic understanding and/or practical skills in terms of:

- **Chemical composition of the Earth's surface** (natural and human-impacted)
- **Basic analytical techniques, and modern methods, applied in geochemistry**
- **Chemical processes and reactions that govern the composition of rocks, minerals, soils, and natural waters** (oceans, rivers, lakes)
- **Global elemental cycles (e.g. carbon), and their impact on the Earth's environment**
- **Issues of ongoing human-induced global environmental changes** (e.g., acid rain, ocean acidification, metal pollution, water contamination, etc.)
- **Application of isotopes for tracing of the sources, contamination, and transport of certain chemicals and compounds in the environment**
- **Hands-on skills in field methods for sampling and analysis** (collection of waters, pH, alkalinity, fluoride), **and simple geochemical modeling** (mixing, tracing, etc.)

Course Syllabus – Our time plan for lectures, practicals, etc.

Oct 15 (WED)

Lectures: Introduction, Basic concepts in geochemistry: Reactions, Chemical units, Composition of earth's system components (e.g., crust, oceans, atmosphere)

Lectures: Analytical methods for elements and isotopes, **Geochemistry of solids** (rocks, minerals, soils, etc.), Quantification of analytical data & basic calculations

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Oct 16 (THU)

Lectures: Aqueous geochemistry, Composition of natural waters, Concepts of: Activity, Solubility, Mineral saturation state, basic calculations

Lectures: Environmental isotope geochemistry (radiogenic and stable isotopes) Expression of isotope composition, Practical examples from oxygen isotopes and chromium isotopes (e.g. tracer of toxic metal contamination in waters)

Course Syllabus – Our time plan for lectures, practicals, etc.

Oct 17 (FRI) **Lectures:** **Biogeochemistry of global carbon cycle,** Basics of 'carbonate system' in natural waters (pH, alkalinity, buffer capacity, etc.), Acid-base titration, implications for current environmental issues (acid rain, soil/ocean acidification)

Practicals: Hands-on measurements of '**carbonate alkalinity**' in natural waters via **acid-based titration**, data interpretation, and basic calculations

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Oct 18 (SAT) **A spare day:** A possibility for further lectures on **Basics of geochemical modeling**, the application of isotope tracers, mass-balance calculations, etc.

Oct 19 **A free day** (SUN)

Oct 20-22 (Mon/Tue/Wed)**:** **Field practicals** (3 groups, and each day for 1 group): Calibration of our analytical systems and devices (hand-meters, probes, and kits) for the **field measurements of pH, Eh, Alkalinity, and fluoride concentration (F-)**

Oct 23 (THU) **Practicals:** Processing and evaluation of field-obtained data, and final tests

Devices used for our field-practicals ....

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GHM pH-meter with
Calibration buffers

HANNA Multi-meter
with fluoride (F^-) probe

HACH Alkalinity
Test Kit

Syringe with membrane filter

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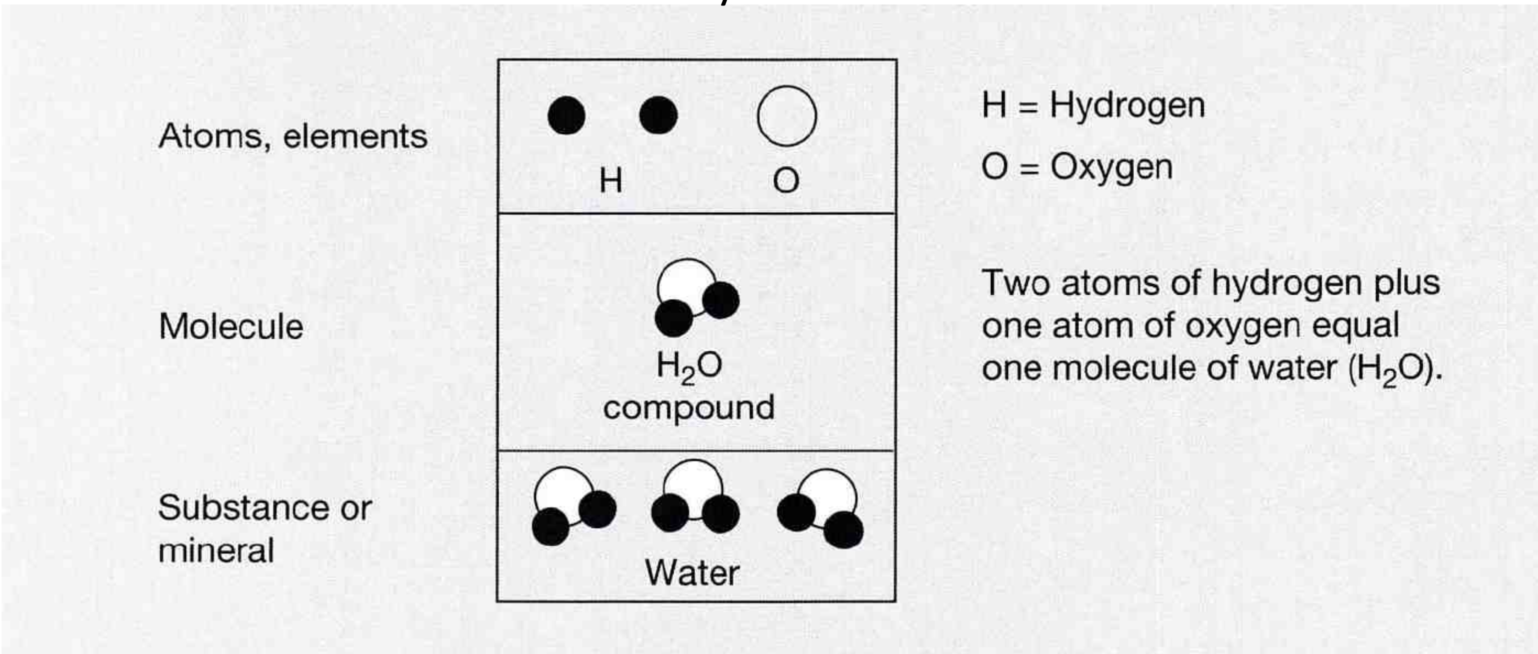
Basic Concepts in Geochemistry

LECTURE 1: Arba Minch, Ethiopia, Oct 15, 2014

Geochemical Building Blocks

Atom – is the smallest, i.e. basic, particles that can enter into a chemical reaction

Elements – consist of atoms of the same kind and when pure they cannot be decomposed by chemical reactions. There are 118 known chemical elements, 94 occur naturally on Earth and other 24 elements are artificially created.



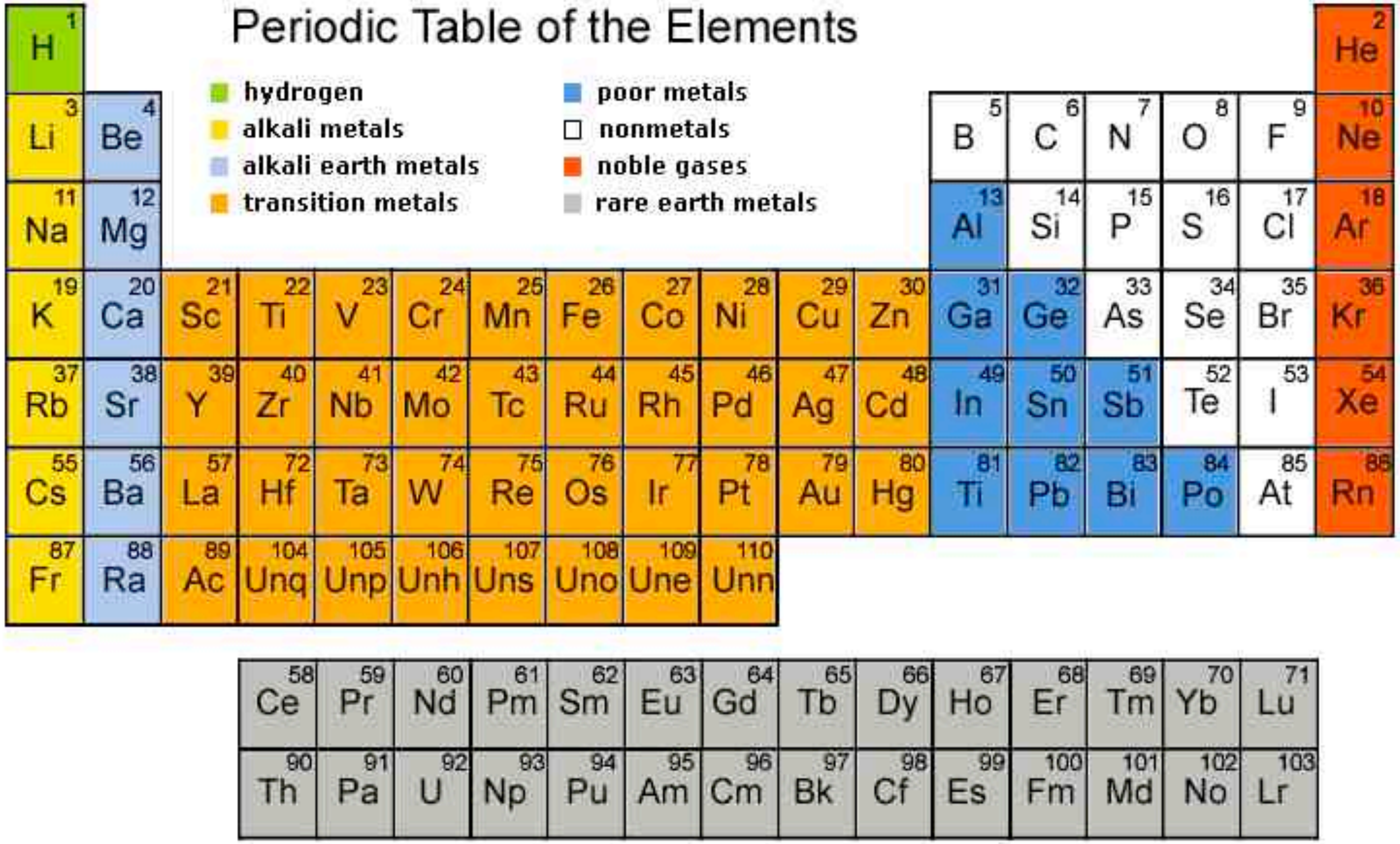
Compound – is formed when two or more atoms of the same or different elements are bonded, or combined, in a definite proportion

Molecule – is the smallest particle of a compound that can exist and exhibits specific properties of that compound

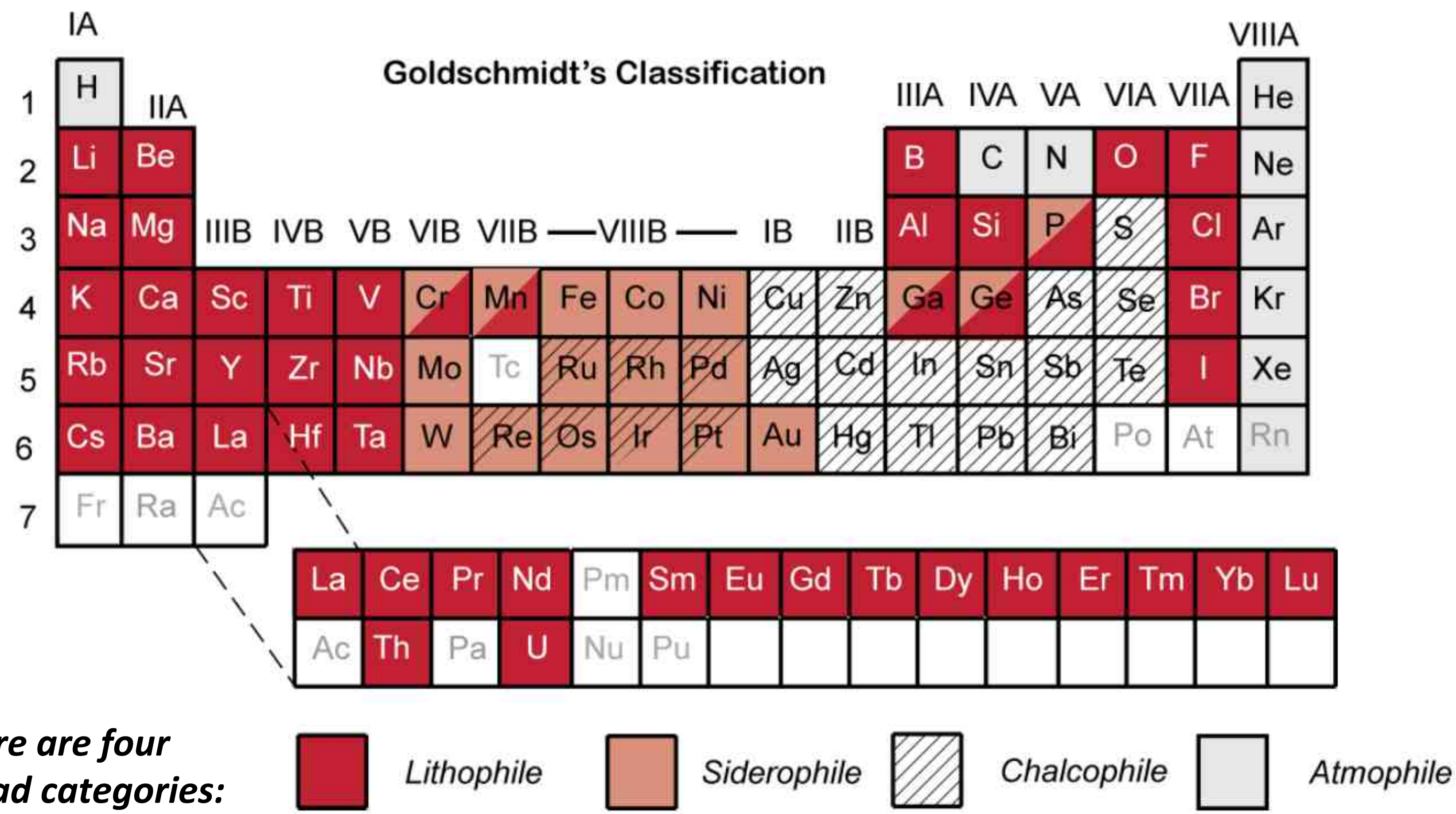
Periodic Table of Elements – Mendeleev Classification (1869)

Groups →

Periods ↓



Geochemical Classification of Elements (Goldschmidt, 1923)



There are four broad categories:

Lithophile – show an affinity for **silicate phases**, and thus are concentrated in Earth's **crust and mantle**

Siderophile – have an affinity for **metallic liquid phases**, and thus are concentrated in the Earth's **core**

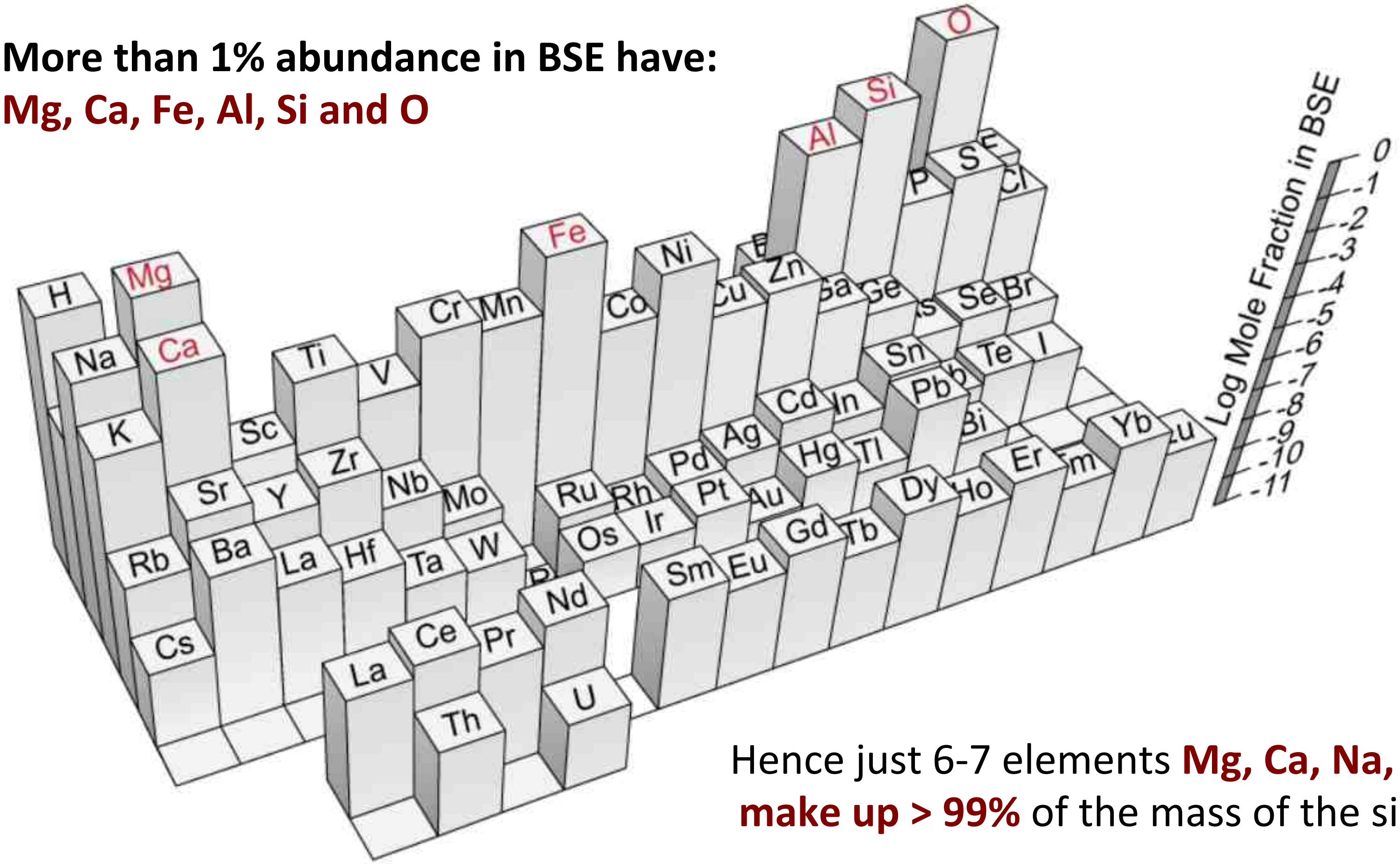
Chalcophile – show an affinity for **sulfide liquid phases**, and thus are more concentrated in the **core**

Atmophile – are **volatile** and thus are more concentrated in the Earth's **atmosphere and hydrosphere**

Concept of Major and Trace Elements

Major elements – are those whose abundance exceeds 1 percent (mol %) of the total mass of elements present in the Earth's silicate reservoirs (= crust and mantle).

More than 1% abundance in BSE have:
Mg, Ca, Fe, Al, Si and O



Hence just 6-7 elements **Mg, Ca, Na, Fe, Al, Si, O make up > 99%** of the mass of the silicate Earth

The remaining ones (though sometimes locally concentrated) are considered ***trace elements***

Expression of the Element Concentration

<u>Concentration of the element by mass</u> (%, ppm, ppb, ppt):

x 1000 000 000 000 (**ppt**)

x 1000 000 000 (**ppb**)

x 1000 000 (**ppm**)

$$\textit{Percent by mass (wt\%)} = \frac{\textit{a mass of the element}}{\textit{a total mass of solution}} \times 100\ (\%)$$

<u>Molar concentration of the element</u> (mol/L, mol/kg):

First, we need to calculate how many **moles** of the element are present in the solution.

One **mole** of the element contain **6.0221415 x 10^{23}** atoms of this element, **Avogadro's No.**

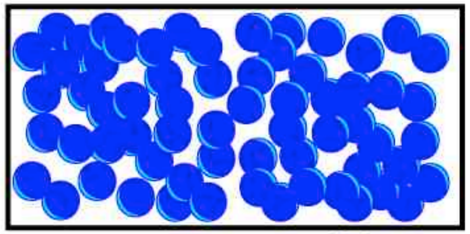
For example the molar mass of Carbon is 12.01 grams per one mole (= 6.02 x 10^{23} atoms)

$$\textit{Molar concentration (mol/L)} = \frac{\textit{moles of the element}}{\textit{Liters of a solution}}$$

Molar masses of elements – Examples

<u>Molar concentration of the element</u> (mol/L, mol/kg):

1 mole of any substance



has 6.023 X 10^{23} atoms

Examples:

Hydrogen (H) = 1.0079 g / mol

Carbon (C) = 12.0110 g / mol

Oxygen (O) = 15.9994 g / mol

Chlorine (Cl) = 35.4527 g / mol

Basics of Chemical Reactions

Let's consider a simple chemical reaction: $A + B \rightleftarrows C + D$

The rate of the forward reaction (r_f) can be defined as: $r_f = k_f (A)*(B)$

And the rate of the backward reaction (r_b) b is then: $r_b = k_b (C)*(D)$

where ***(A)***, ***(B)***, ***(C)***, and ***(D)*** are the concentrations of the elements, or compounds and $k_{f,b}$ are the proportionality or rate constants (i.e. a relationship between "*reaction rate*" and "*concentrations of reactants*")

At equilibrium conditions: $r_f = r_b$ or $k_f (A)*(B) = k_b (C)*(D)$

Which can be rewritten as:

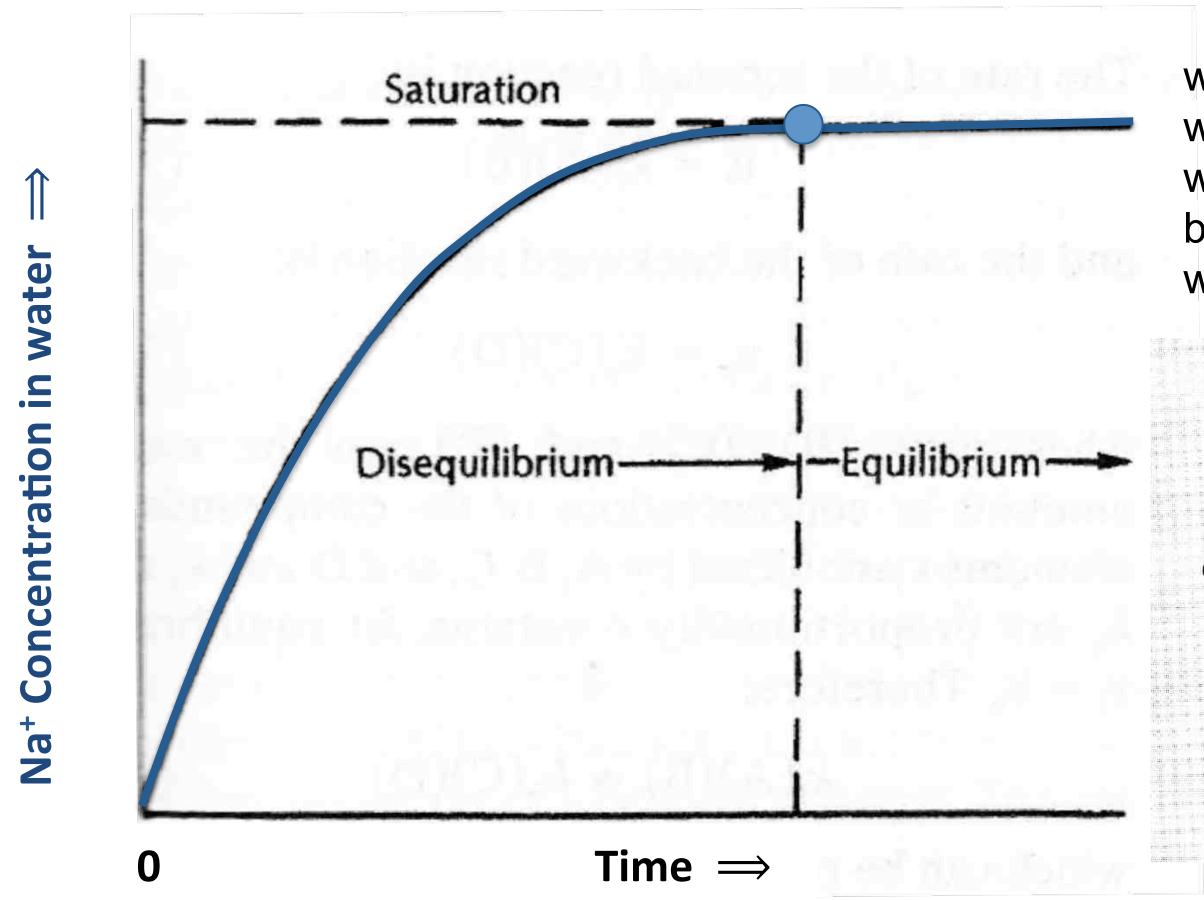
$$\frac{k_f}{k_b} = \frac{(C)*(D)}{(A)*(B)} = K$$

where K is the ***equilibrium constant*** for this reaction

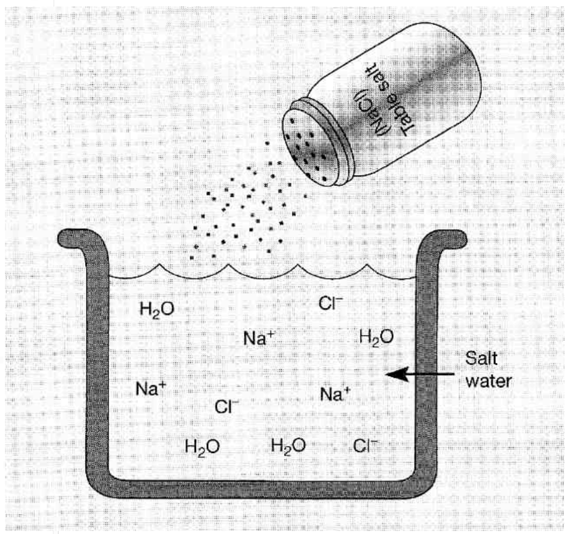
Basics of Chemical Reactions

An example of a simple chemical reaction that achieves an equilibrium state:

$NaCl \rightleftarrows Na^+ + Cl^-$ sodium chloride (table salt) being dissolved in pure water



when no more NaCl would dissolve in water the solution became ***saturated*** with respect to NaCl



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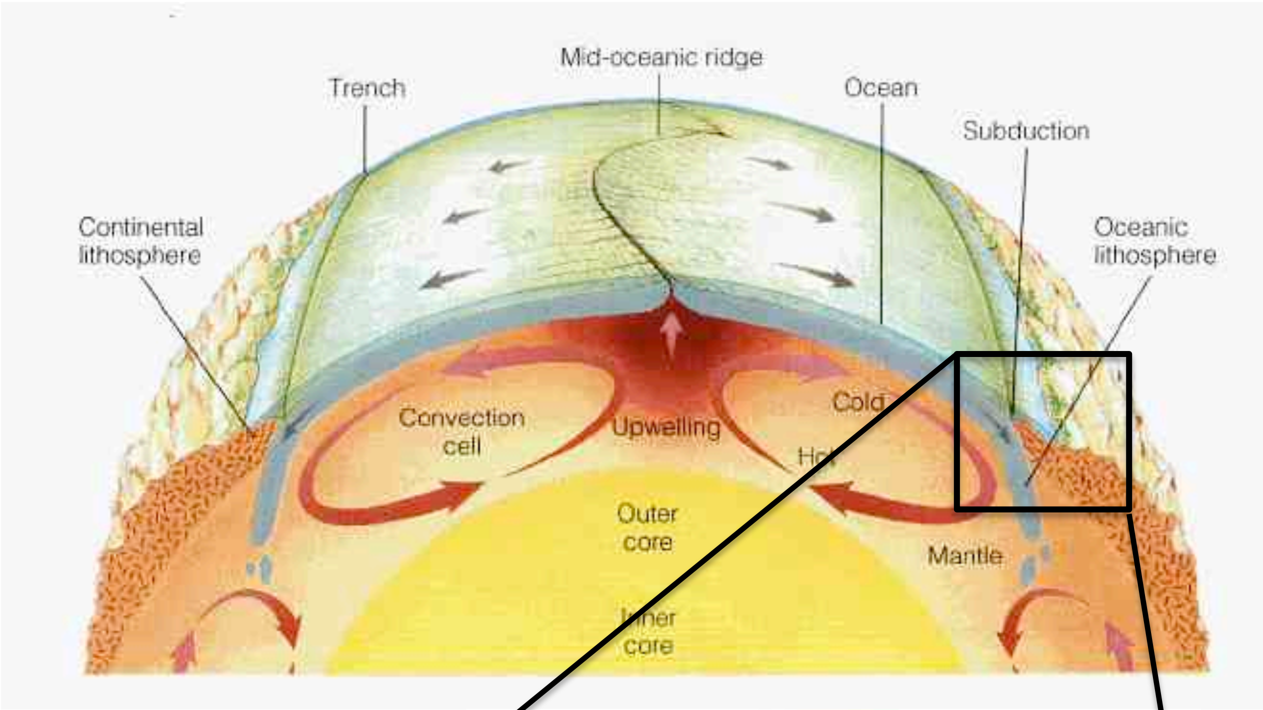
Geochemistry of Solid Earth's Materials

LECTURE 2: Arba Minch, Ethiopia, Oct 15, 2014

Plate Tectonics and Chemical composition of Earth crust



Source: Earth Systems, Kump 2011

Oceanic crust

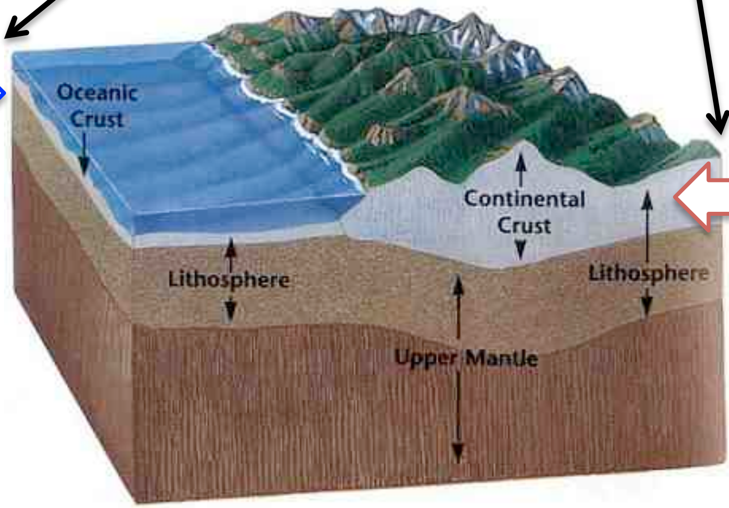
Density of **2.9 g/cm³**

Less SiO_2 (< 55%)

Ca, Mg, Fe rich

Mafic rock types:

Basalts (dark)



Continental crust

Lower density of **2.7 g/cm³**

More SiO_2 (> 65%)

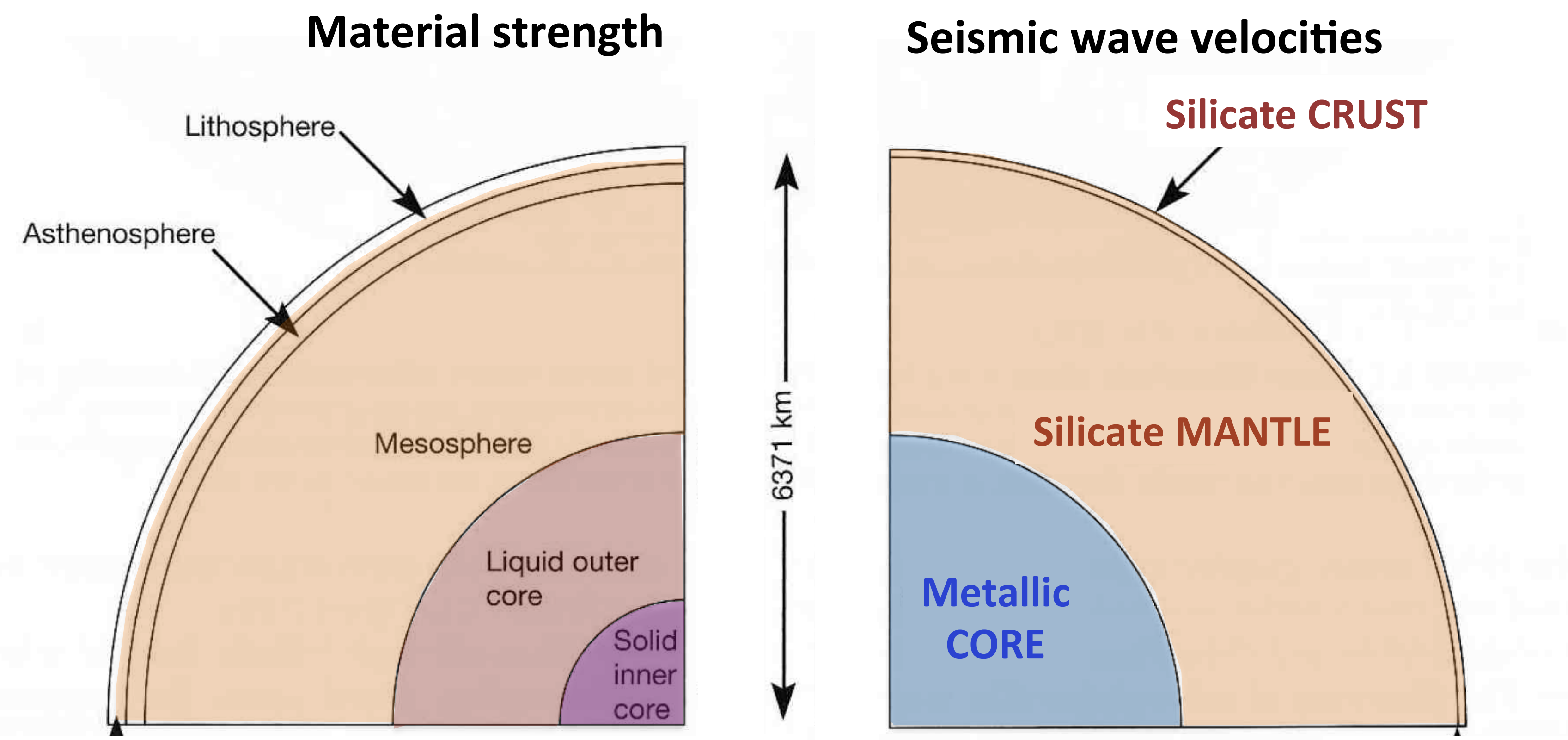
Na, K, Al rich

Acidic rock types:

Granites (light color)

Internal structure of the Earth

Classifications based on:

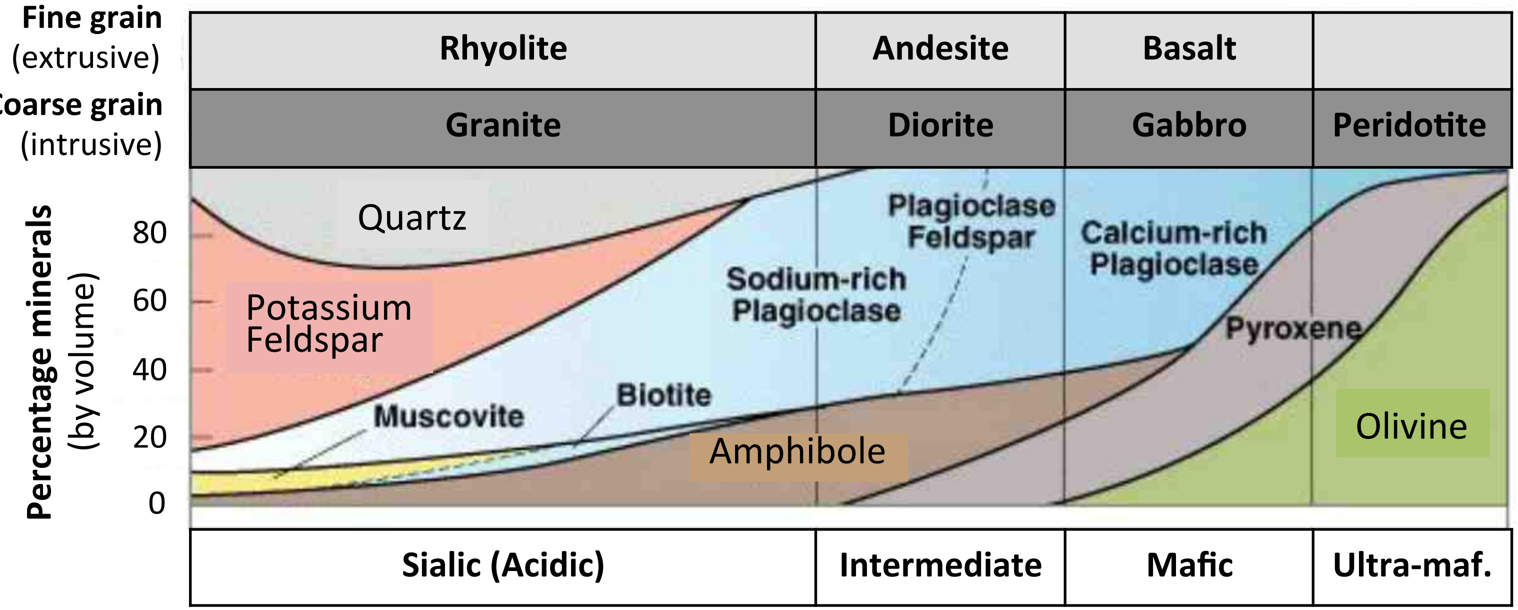


Our planet Earth is composed of chemically distinct reservoirs outer **silicate crust + mantle,** and inner **metallic core**

Silicate = composed mostly of silica and oxygen (SiO_2 groups)

Metallic = enriched in iron, nickel, chromium (heavy metals: Fe, Ni, Cr)

Classification of Silicate Igneous Rocks



Increasingly darker color of rocks

2.65 g/cm^3 Increasing density 3.3 g/cm^3

600 °C Increasing temperature of crystallization 1200 °C

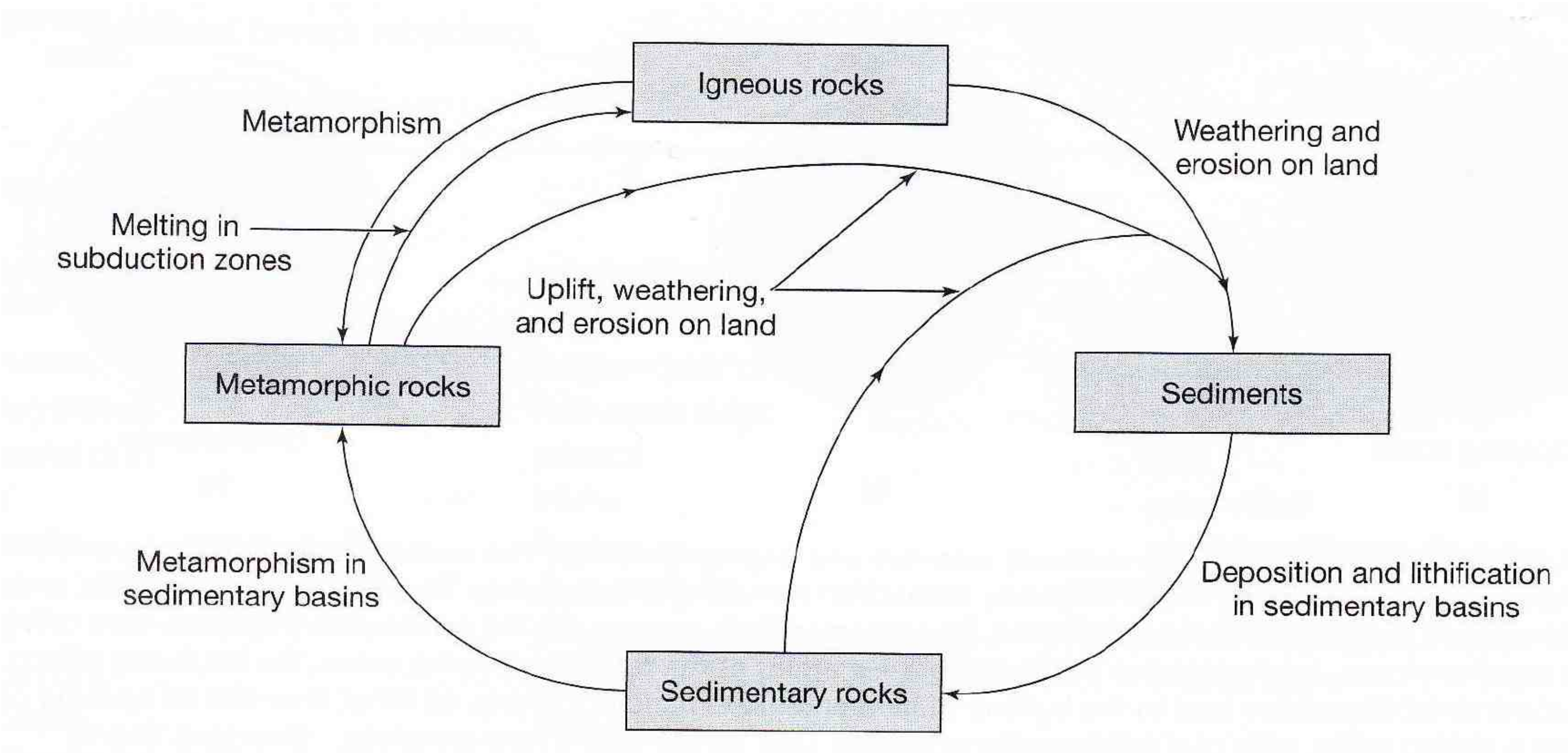
Increasing calcium, magnesium, and iron

Increasing potassium, sodium, and aluminum

Increasing silica content

The Rock Cycle and Weathering

Rocks (i.e. aggregates of minerals) are continuously being recycled by plate tectonics, and a complete regeneration of the rocks on Earth, **the rock cycle**, takes about 100 Ma



Igneous rock
These rocks are formed when magma (molten rock) from the Earth's interior cools and solidifies.

Metamorphic rock
The heat and pressure of the Earth's interior transform igneous and sedimentary rocks into metamorphic rocks.

Sedimentary rock
Atmospheric agents erode and transport igneous rocks to the seabed, where they are compressed and merged with others into sedimentary rocks.

Further Classification of Rocks

Igneous

- Intrusive
  - Granite
  - Granodiorite
  - Diorite
  - Gabbro
  - Peridotite
- Extrusive
  - Rhyolite
  - Dacite
  - Andesite
  - Basalt

Sedimentary

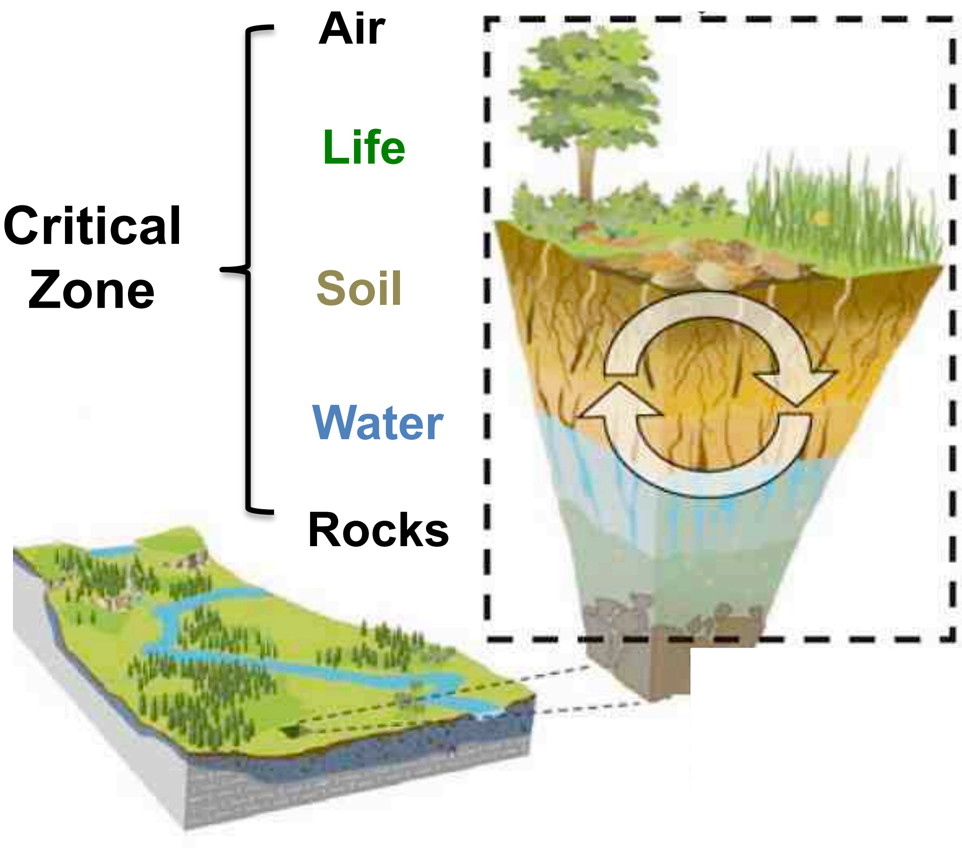
- Clastic
  - Sandstone
  - Siltstone
  - Mudstone
  - Shale
- Chemical
  - Limestone
  - Dolostone
  - Evaporites
- Biologic
  - Coal
  - Chert

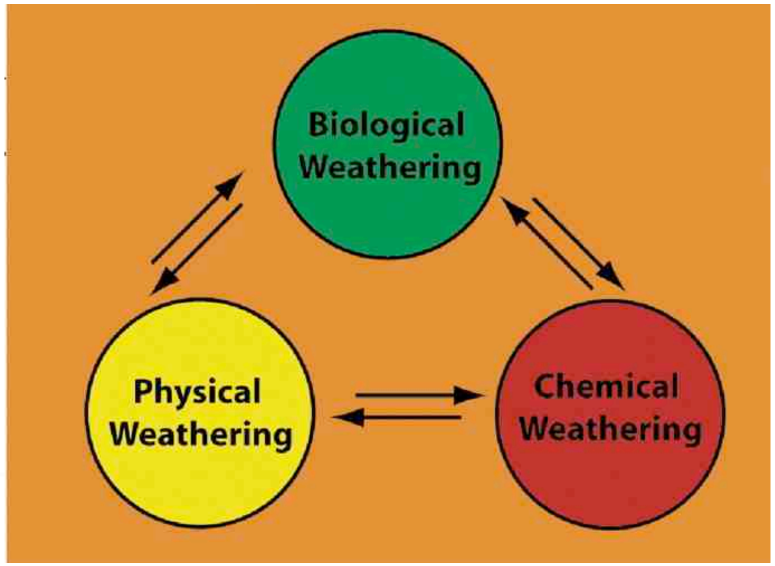
Metamorphic

- Foliated
  - Slate
  - Schist
  - Gneiss
- Non-foliated
  - Marble
  - Quartzite

Geochemistry of Earth’s Outer Skin - Critical Zone

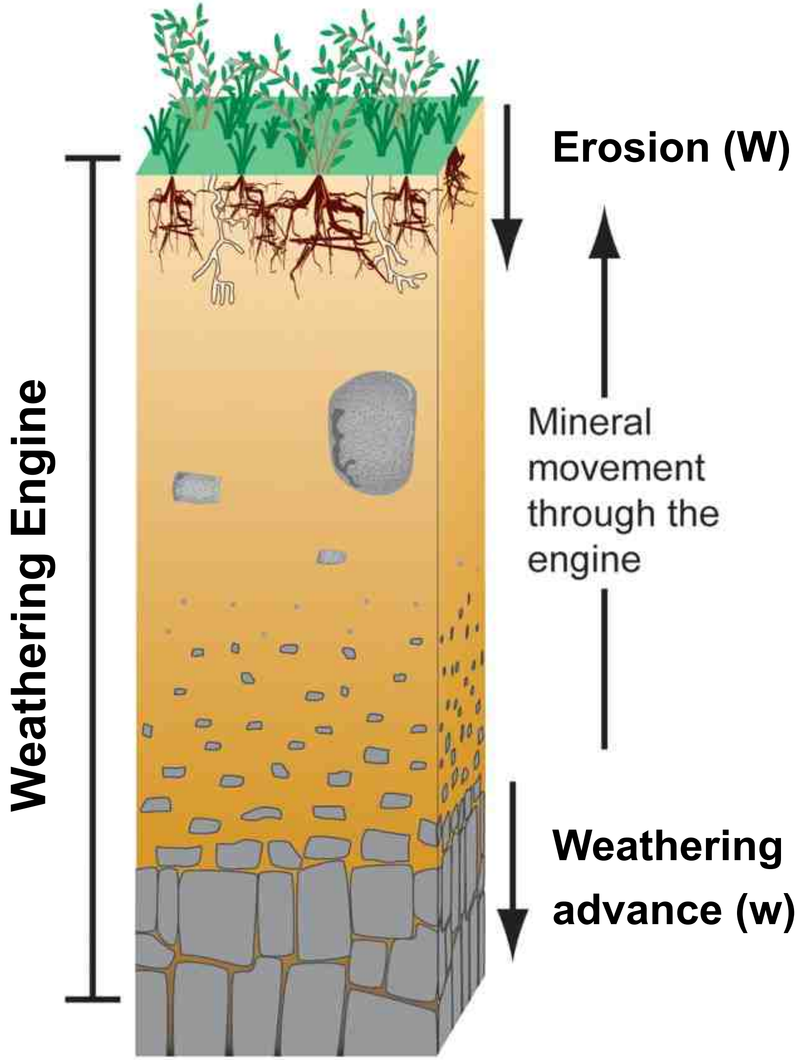
The Critical Zone
is defined as the Earth's outer layer, extending from vegetation canopy to the soil and groundwater. This near-surface environment in which complex interactions involving rock, soil, water, air, and organisms is critical to sustains life on earth.





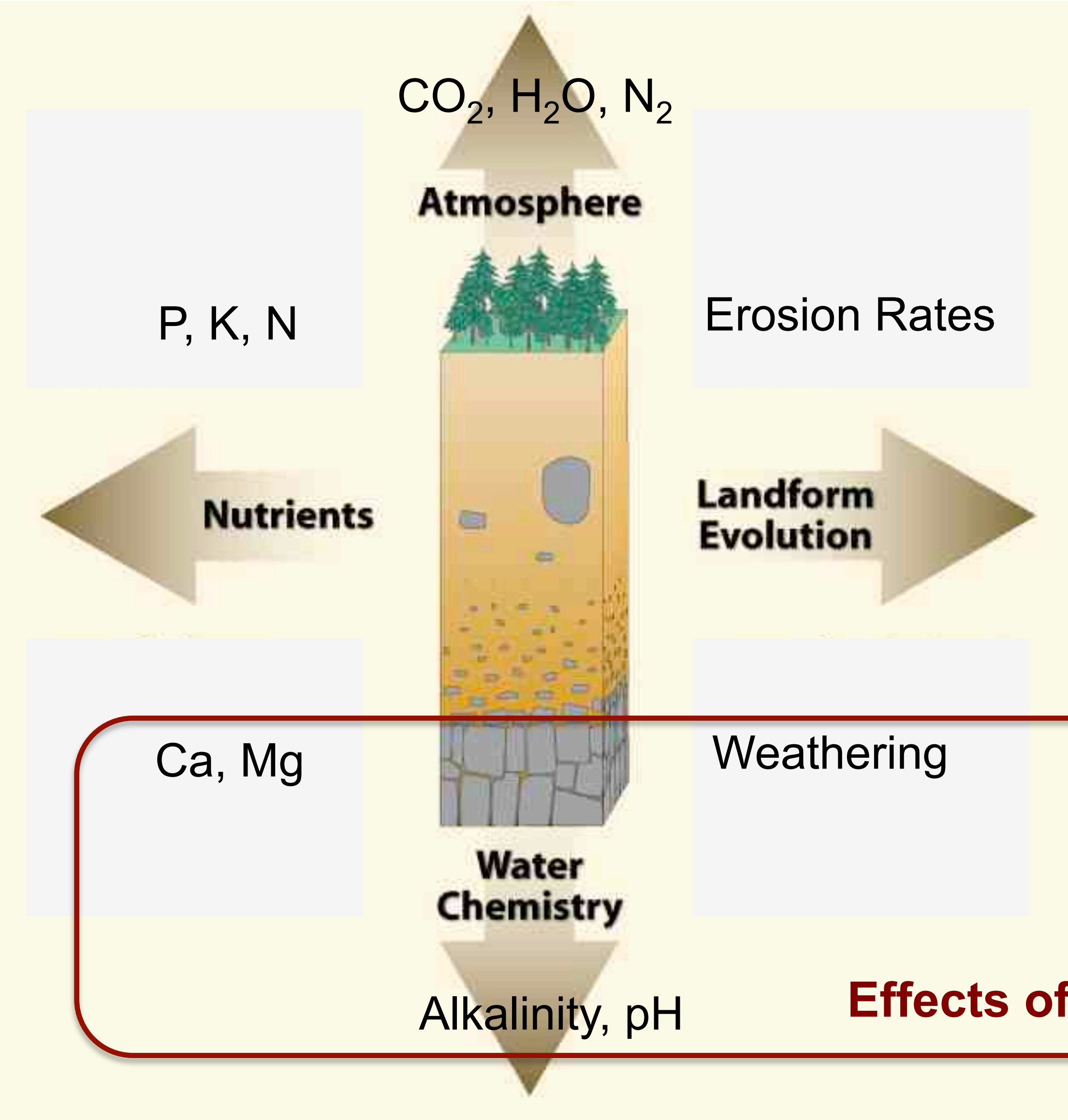
Critical Zone Functions :
Weathering Engine,
Soil Production, Water Storage,
Support of Terrestrial Life

Critical Zone – Earth's Weathering Engine



Brantley et al. (2007)

Critical Zone Processes



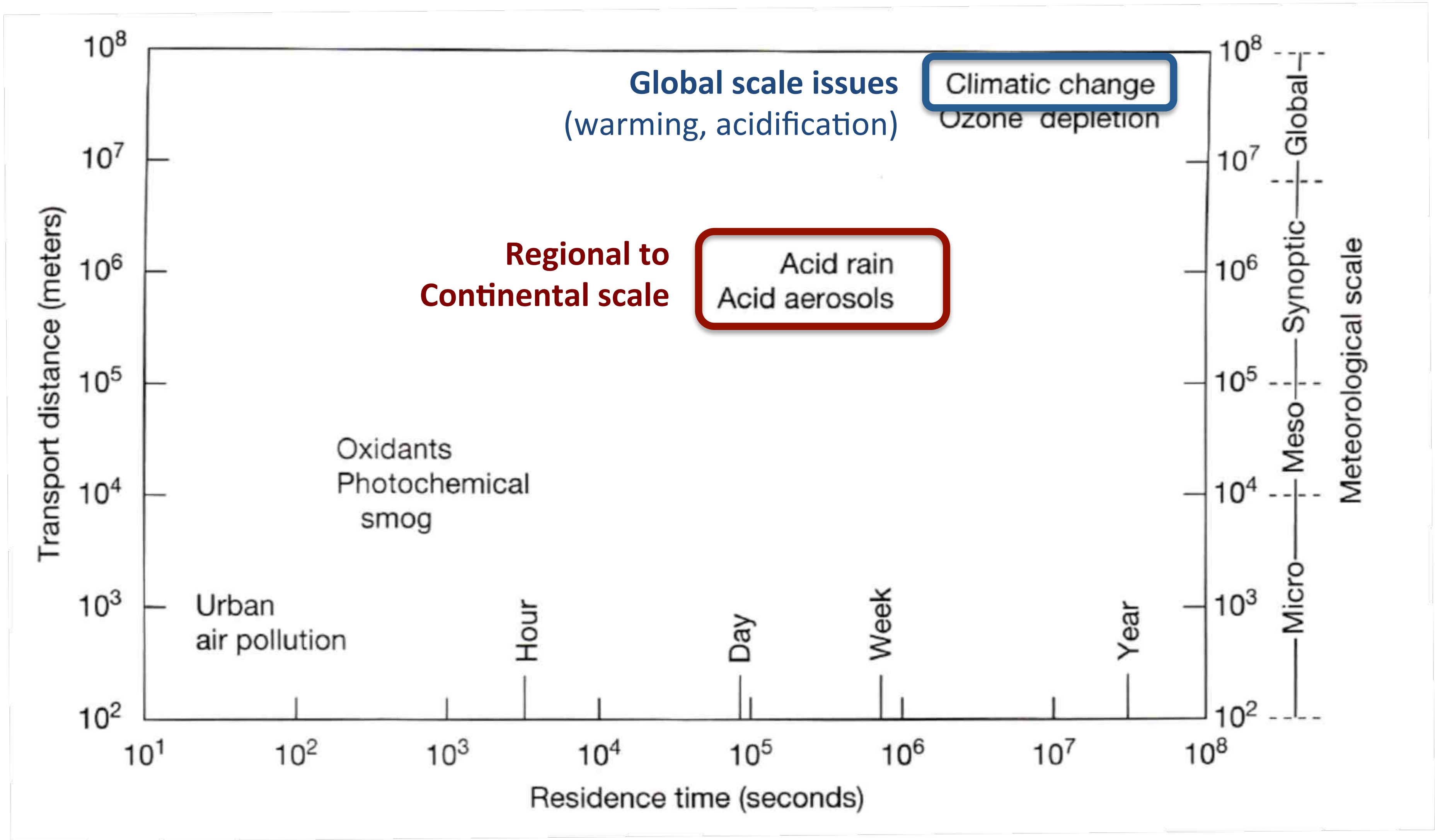
Processes operating within the Critical Zone control for example:

- Exchange of gases between soils, plants and the atmosphere
- Fluxes and availability of major nutrients and base cations (Ca, Mg)
- Chemical composition of soil- and stream-waters

Effects of Anthropogenic Acid Rain

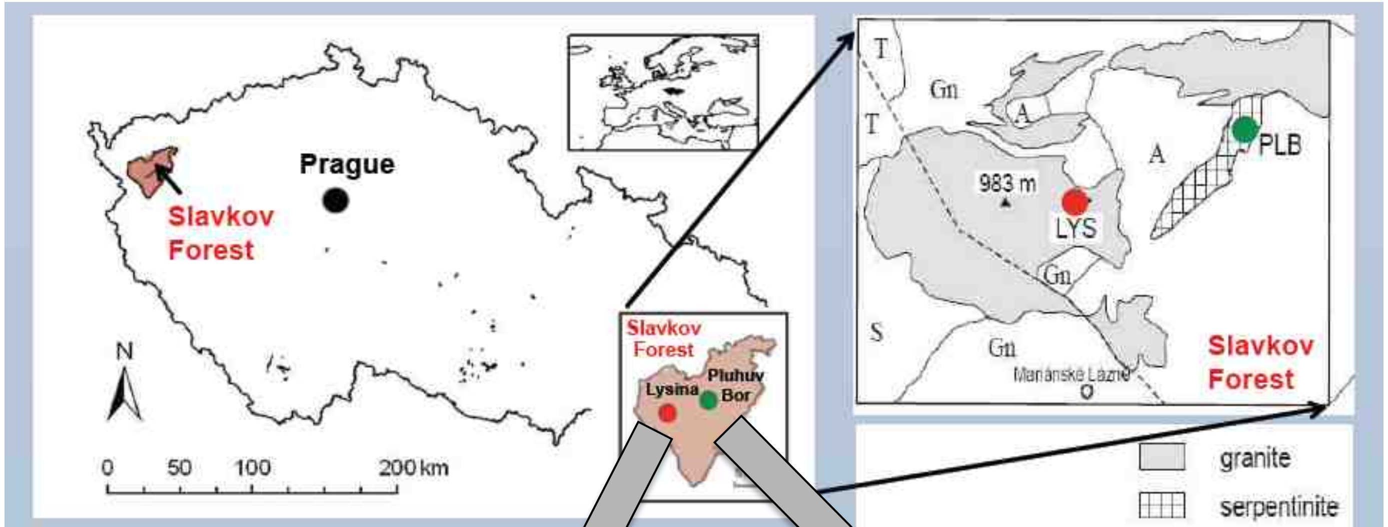
Anthropogenic Acid Rain

Diagram showing two major "air-pollution" issues, operating on different time and space scales



Geochemistry of soils (weathering profiles) at acidified sites

Study site in Czech Republic (west from Prague)



Acidic rock (high SiO_2)

Low: Mg, Ca (high K, Na)

Mafic rock (low SiO_2)

High: Mg, Cr, Ni (low K, Na, Ca)

Geochemistry of weathering profiles at acidified sites

Primary reasons for our geochemical investigations:

- Magnesium (**Mg**) and Calcium (**Ca**) are both **major nutrients** for the forest ecosystems that growth on these sites, and we want to understand their bio-availability and degree of leaching from soils
- **Ca** and **Mg** are also the main **base cations** that neutralize the acidity in soils from human-produced atmospheric acid compounds (acid rain)

- Finally, there are naturally high concentrations of **toxic metals** such as **Cr** and **Ni** in soils at the mafic (serpentinitic) site, which create issues for a forest health
- Thus, we also want to understand how these toxic metals behave in these soils during weathering and biological uptake by plants

Geochemistry of weathering profiles at acidified sites

Description of drill core material by soil scientists and geologists

Photo of core (cca 1 : 10)	Depth from(m)	Field description	Petrology, mineralogy	Samples
	0,0 ◙ 170 mm	Organic soil and brown-gray soil	Organic matter + soil,	
	0,10	residual clays with soil and serpentinite fragments, heterogeneous mixture	Serpentinite + soil + reziduum	
	1,20	grey green clayei to snady residuum with fragments of S	clayey serpentinite + residual mixture	
	1,90	Stony residuum	stony residuum of serpentinite	N 2,59
	3,60	in situ weathered fragments of S	fully serpentinized peridotite with grains and veinlets of secondary magnetite	▶ 4,50 GCH 4,50 N 4,04+ H 3,73

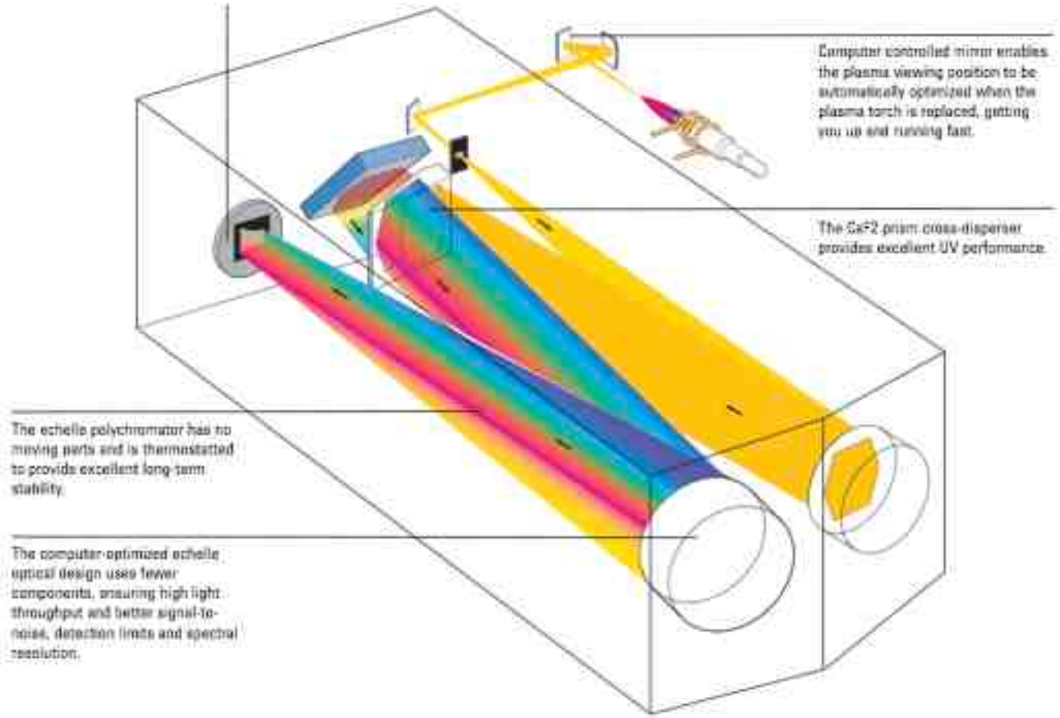
Preparation of drill-core samples for geochemical analysis

Cutting and weighing of selected samples

Close-up view on samples

Dissolution of powdered samples
by acids in metal-free laboratory

Elemental Analysis of powdered and acid-digested samples



Agilent ICP-OES Spectrometer

An **inductively coupled plasma (ICP) spectrometer** is a tool for trace detection of metals in solution, in which a liquid sample is injected into argon gas plasma contained by a strong magnetic field.

Elements become excited and the electrons emit energy at a characteristic wavelength, and emitted light is then measured by optical spectrometry. This method, **optical emission spectrometry (ICP-OES)**, is a very sensitive technique for quantification of elements (dissolved ions) in a sample

Schematic Diagram of ICP-OES Analytical System

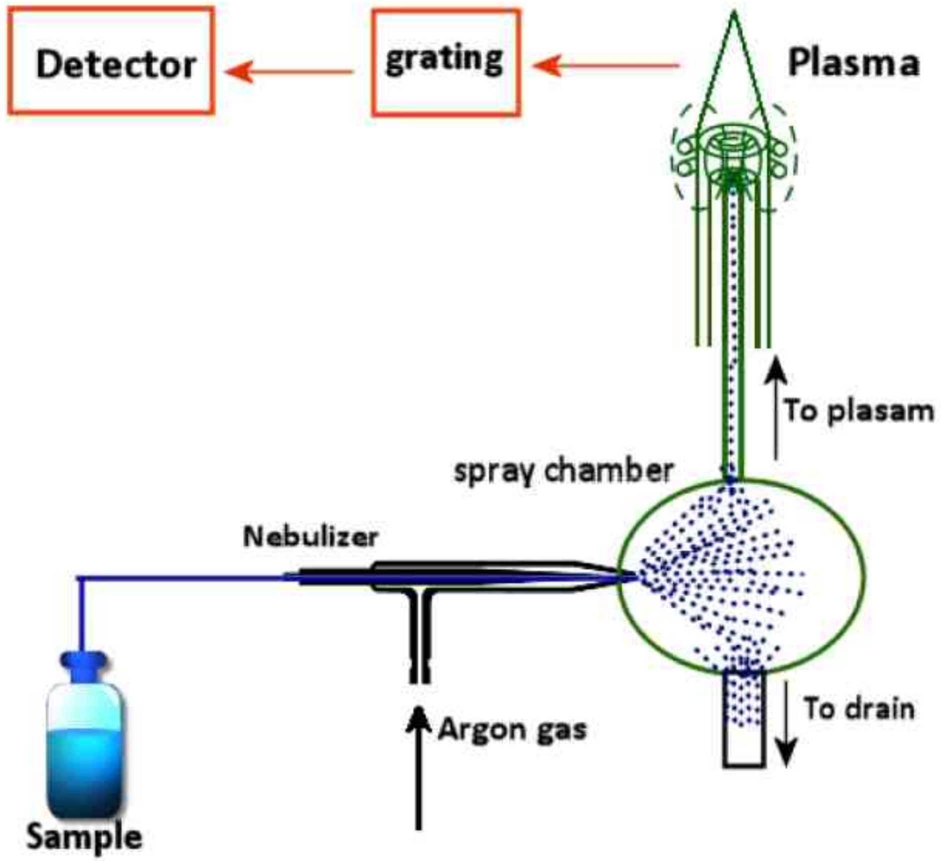


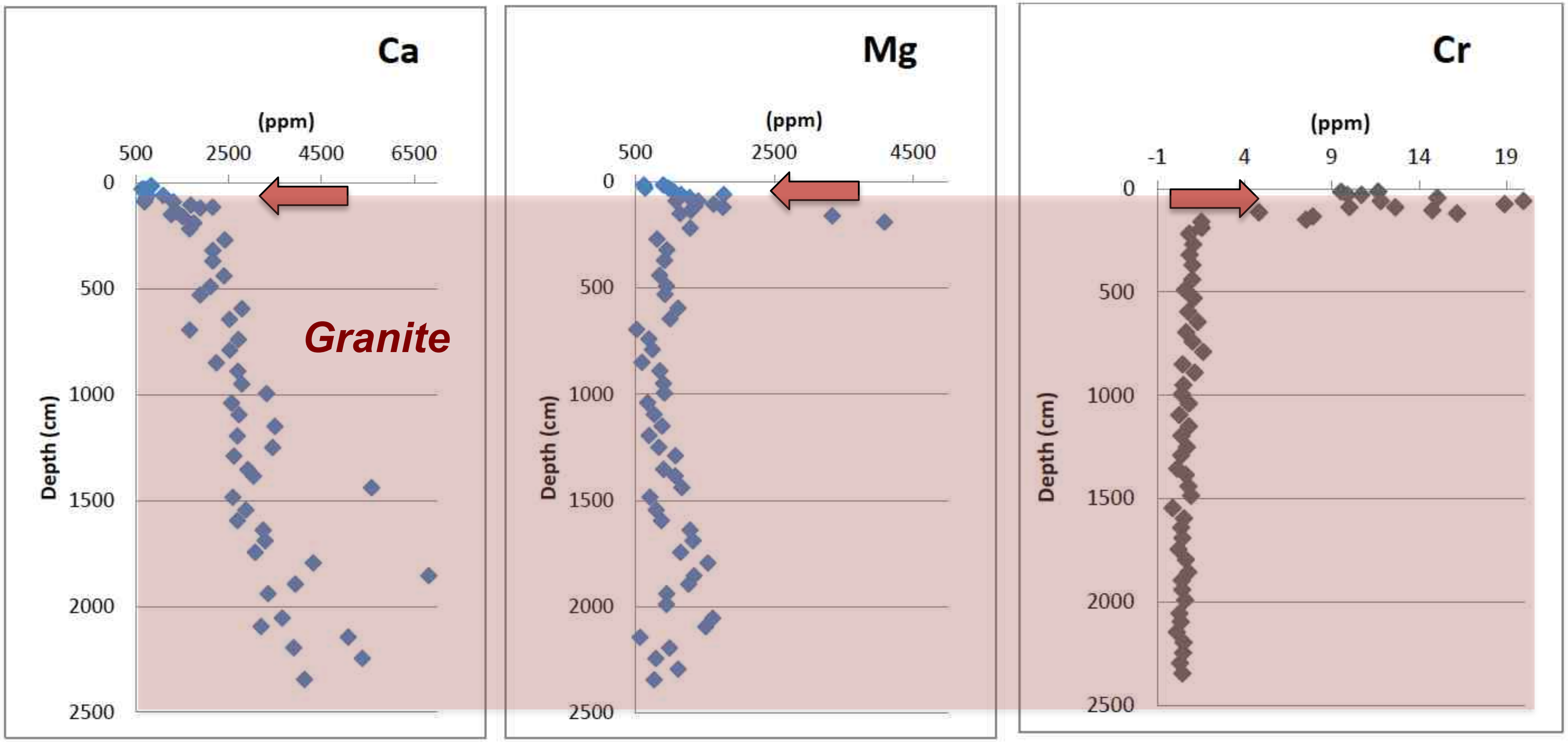
Figure 5 Diagram of sample introduction to ICP-OES (CHEMIASOFT, 2014)

Output data:

Detector will record counts (or signal) for a specific element, and the magnitude of this signal will then corresponds to a concentration of this element in the sample-solution.

Concentration profiles of selected elements from drill cores

GRANITE Bedrock - Concentration of Calcium, Magnesium and Chromium

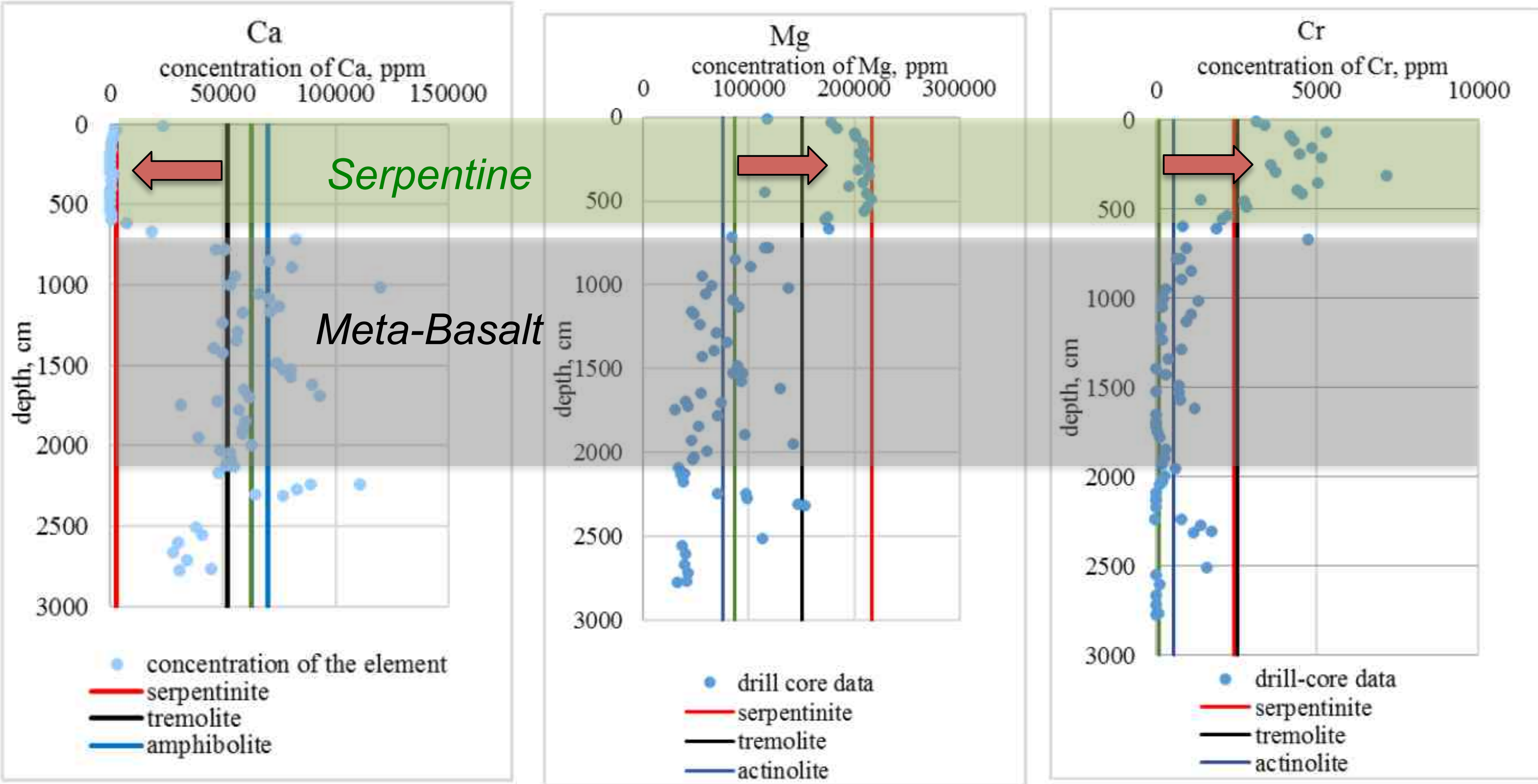


Note that Ca and Mg are both depleted in top soils, while Cr is enriched

Also, geology was 'favorable' as the entire profile is composed of granite

Concentration profiles of selected elements from drill cores

SERPENTINE Bedrock – Concentration trends of Ca, Mg and Cr



Note that in this drill core we have changes of rock types with depth…
But generally, Ca is depleted at the top while Mg and Cr are enriched.

Calculation of 'normalized' elemental profiles (Tau, τ)

Having concentration data, we can now **directly calculate and quantify a degree of leaching** (loss) **or accumulation** (gain) **of certain element** (e.g., nutrient or toxic metal) through the studied weathering profiles

parameter (Tau or τ), are being calculated based on the following relationship (Brantley et al., 2007):

$$\tau_{i,m} = \frac{C_{m,w}}{C_{m,p}} \cdot \frac{C_{i,p}}{C_{i,w}} - 1$$

Typically, titanium (**Ti**) or zirconium (**Zr**) are used for the normalization as **immobile elements**

$$\tau_{\mathrm{Ti,\,Ca}} = \frac{\mathrm{Ca}_{weathered}}{\mathrm{Ca}_{parent}} \cdot \frac{\mathrm{Ti}_{parent}}{\mathrm{Ti}_{weathered}} - 1$$

where C represents the concentrations of immobile (i) or mobile (m) elements in weathered (w) or parent (p) material.

$C_{m,w}$ = Concentration of mobile elements in the weathered sample;

$C_{m,p}$ = Concentration of mobile elements in parent (unweathered) material/sample;

$C_{i,p}$ = Concentration of immobile elements in the parent rock (unweathered) sample;

$C_{i,w}$ = Concentration of immobile elements (e.g. titanium) in weathered rock sample.

Chemical Gradients across Weathering Profile

Possible end-member scenarios for Tau-normalized element depth profiles

Depletion Profiles

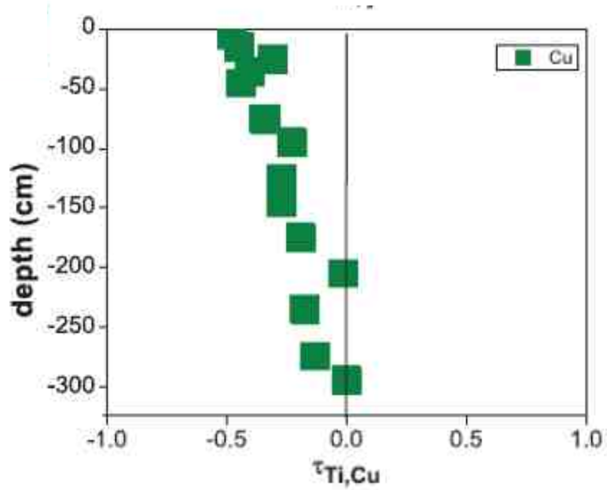
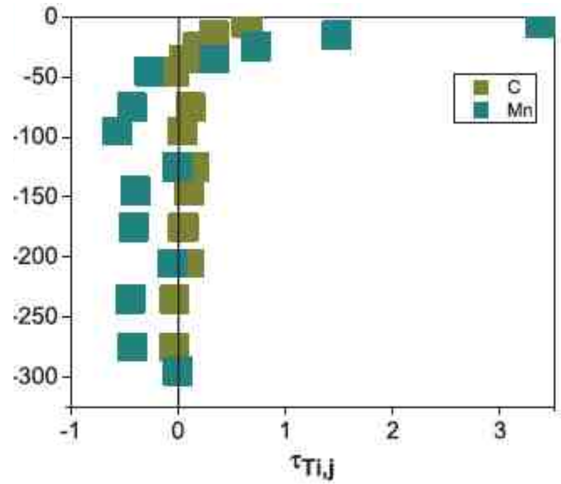


Exhibit depletion at the top due to leaching or biological uptake, which then grades downward

Addition Profiles



Show enrichment from external input at the top grading to the parent concentrations at depth

Biogenic Profiles

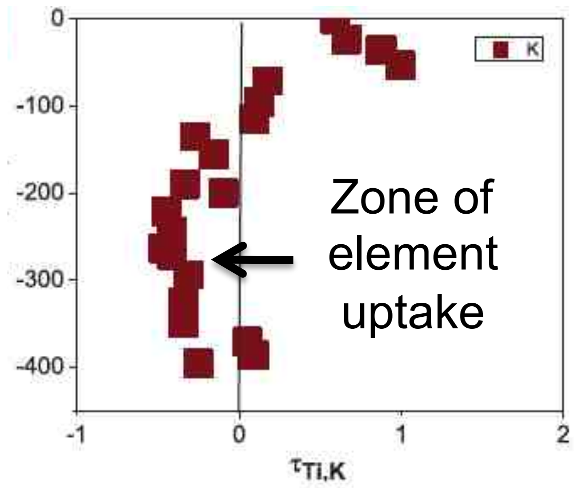
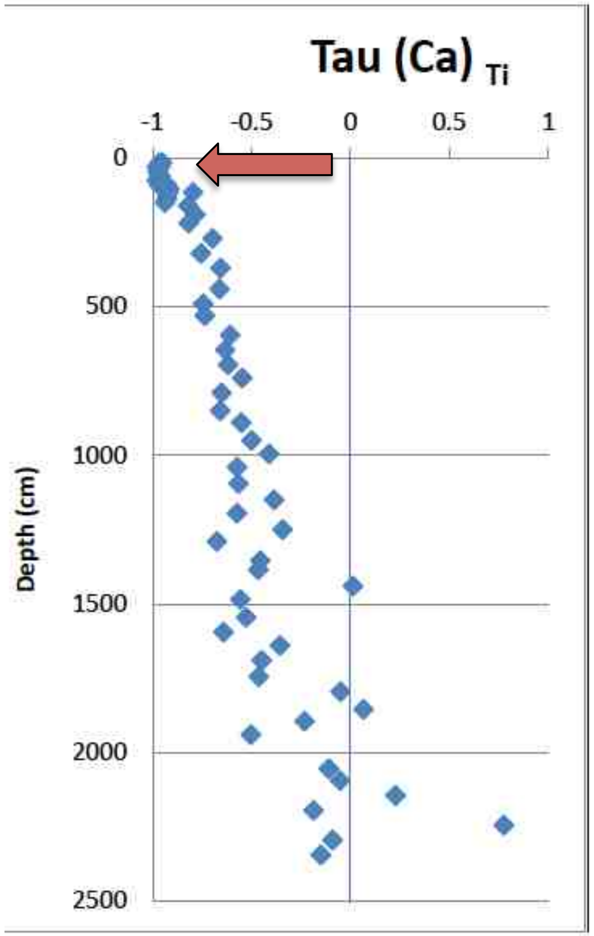


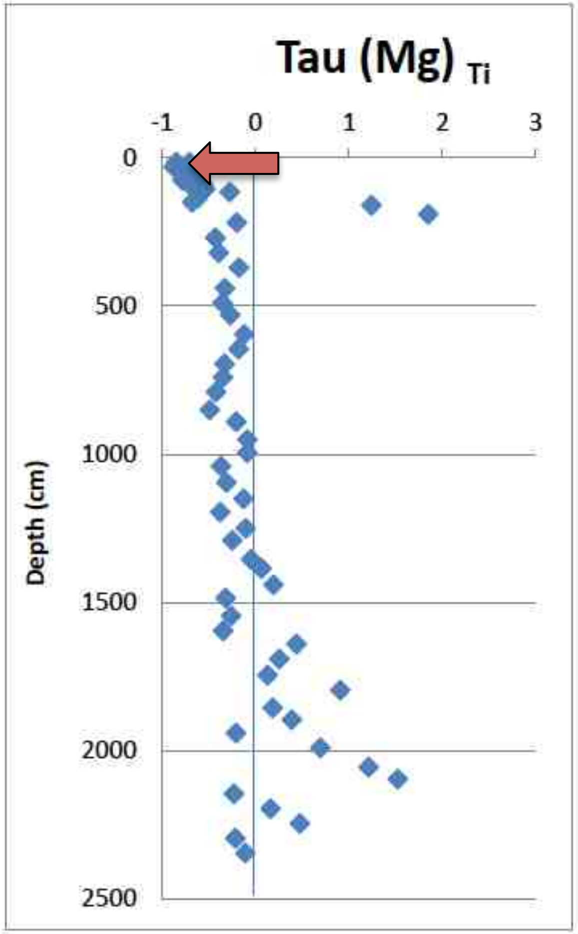
Exhibit enrichment at the top and depleted zone that grades downward to parent concentrations

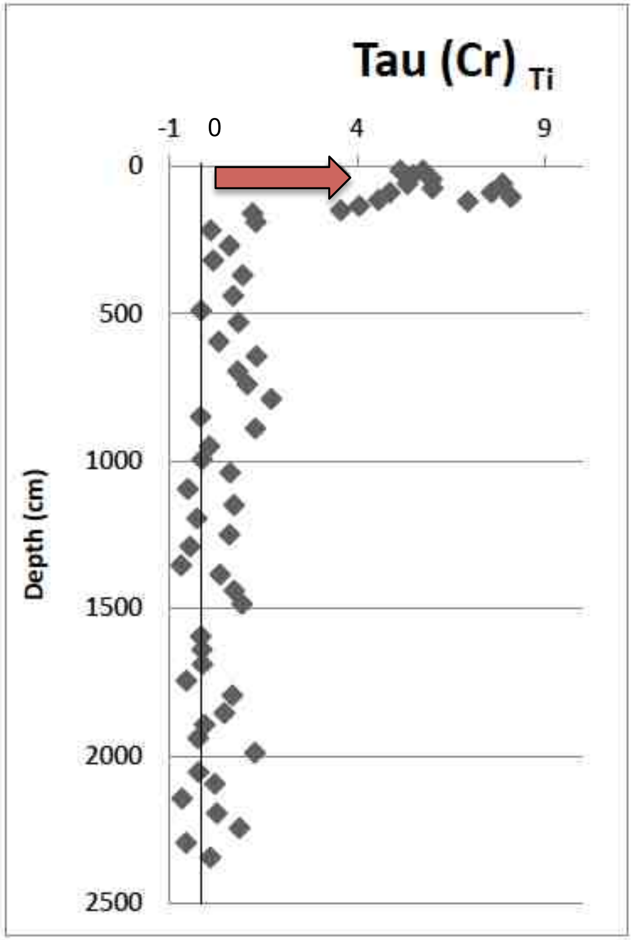
Brantley et al. (2007)

Tau-normalized elemental profiles from our GRANITIC site

Tau = -1 (100% loss) **Tau = 0** (no loss or gain) **Tau = +1** (100% gain)





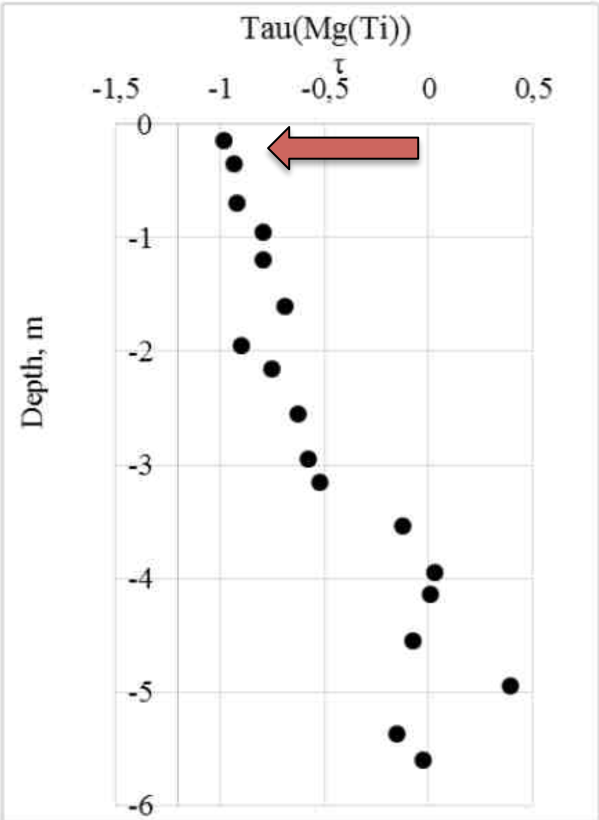


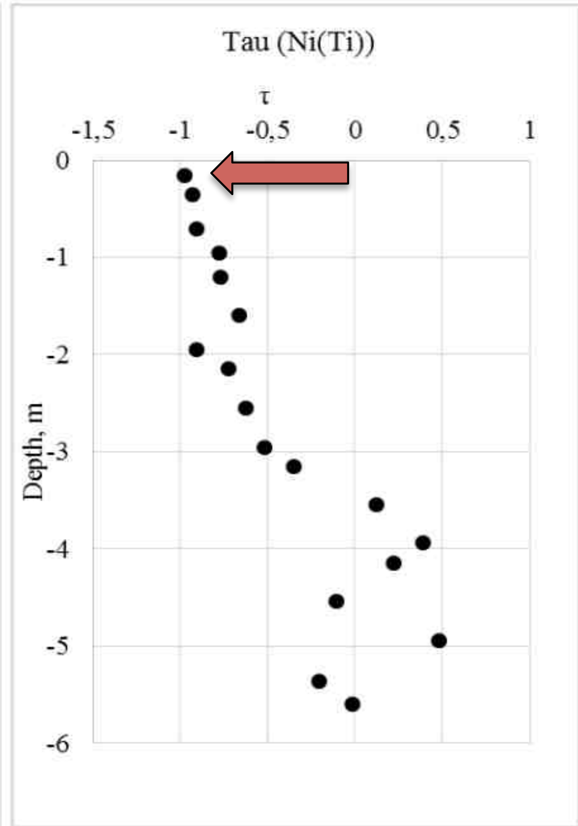
Granite bedrock

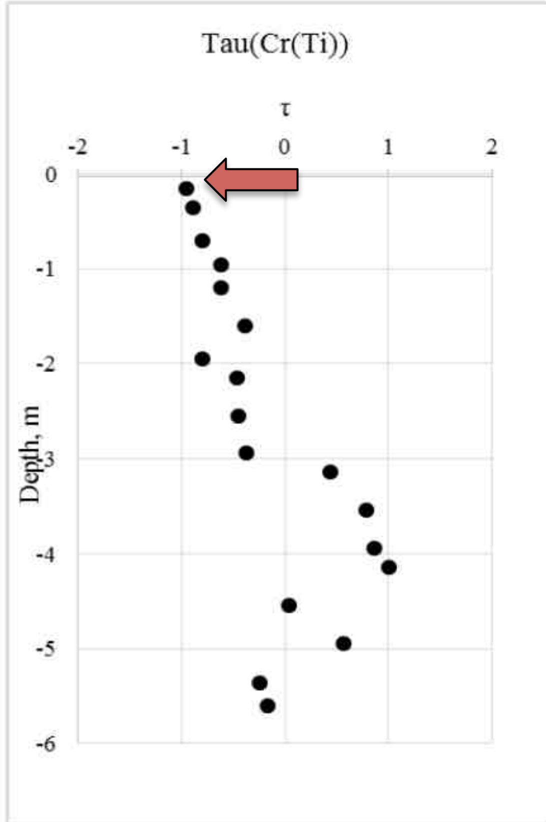
Ca and Mg were heavily leached (~90% loss) from soils

Tau-normalized elemental profiles from SERPENTINE site

Tau = -1 (100% loss) **Tau = 0** (no loss or gain) **Tau = +1** (100% gain)







Mg, Cr and Ni were significantly leached from soils

Calculation of Tau-normalized elemental profiles from data

Depth	Ca(ppm)in Rock	Tau (Ca) Ti	Mg(ppm)in Rock	Tau (Mg) Ti	Cr(ppm)in Rock	Tau (Cr) Ti	Ti(ppm)in Rock	Tau (Ti) Ti
15	838,4095415	-0,951045465	902,8421625	-0,703100748	9,529335624	5,756370108	1010,156311	0,000577287
30	693,6729292	-0,962475094	978,7186649	-0,701816716	9,883979861	5,492482851	1090,336199	0,000577287
60	748,504297	-0,96685365	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
90	685,630007	-0,966835717	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
115	2154,21883	-0,794943503	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
160	1506,078431	-0,820163705	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
190	1749,969067	-0,783316318	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
218	1656,674159	-0,817120575	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0,000577287
270	2419,106593	-0,696793041	811,4601406	-0,42718827	1,052151318	0,60131382	470,588318	0,000577287
320	2159,97463	-0,755367297	953,7243534	-0,391655918	0,852228693	0,172022918	520,7861646	0,000577287
370	2159,023702	-0,656402477	919,9086759	-0,175486292	1,012111642	0,955848103	370,6232734	0,000577287
440	2400,158267	-0,661348539	848,9628483	-0,325375188	0,994057413	0,703094045	418,0345992	0,000577287
490	2107,289228	-0,743869514	948,7891463	-0,350517601	0,57503538	-0,151316455	485,2752867	0,000577287
530	1885,557408	-0,735463576	926,1063501	-0,268242585	1,081117707	0,841758943	420,4163364	0,000577287
595	2786,369143	-0,607795821	1113,783932	-0,117052126	0,773952354	0,322823433	419,0363867	0,000577287
645	2518,847317	-0,633011201	999,6037997	-0,179762886	1,313912468	1,324510374	404,8315351	0,000577287
695	1660,627707	-0,618430874	518,5725556	-0,328925049	0,652783989	0,821312761	256,6991044	0,000577287
740	2709,206013	-0,546600727	694,0315341	-0,345848196	1,019175901	1,07110455	352,4410719	0,000577287

$$\tau_{Ti,\,Ca} = \frac{Ca_{weathered}}{Ca_{parent}} \cdot \frac{Ti_{parent}}{Ti_{weathered}} - 1$$

2095	3198,983606	-0,051789784	1513,093814	1,525916691	0,338530293	0,218440262	198,9906571	0,000577287
2145	5079,157131	0,228556331	566,8798505	-0,227755191	0,115669374	-0,660268435	243,8495037	0,000577287
2195	3903,175447	-0,186005914	991,0814937	0,164053912	0,500566803	0,267591474	282,8278193	0,000577287
2245	5383,43307	0,776096142	794,7583548	0,47673581	0,467165	0,87150736	178,7796772	0,000577287
2295	7260,468942	-0,090522148	1116,224512	-0,212519947	0,296985054	-0,548272908	470,8665573	0,000577287
2345	4136,831965	-0,149291781	770,5385797	-0,107583302	0,438698038	0,095449922	286,8220618	0,000577287

Depth	Ca(ppm)in Rock	Cr(ppm)in Rock	Ti(ppm)in Rock
	5170,977356	0,425853724	304,8240289

‘**Parent**’ bedrock value (least weathered rock)

Calculated and plotted Tau-normalized elemental profiles