Geochemistry

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Phone

Timing

Food

Beverage
• Lectures
• Tuesday: 12.00 am-2.00 pm (Mauritz Béla Hall)
• Sept 10, 17, 25, Oct 2, 9, 16, 23, 30, Nov 6, 13, 20, 27, Dec 4, 11
  (14-(4+3))

• Oral exam
  when: Dec 18 (MSc), Jan-Febr (PhD) (12.00 am - 2.00 pm)
  where: Mauritz Béla Hall (LRG)

• Close semester: 2019, Febr 1. 12.00 pm
Introduction:

Object of geochemistry:

- Chemistry of the Earth as all and its spheres (atmosphere, lithosphere, crust, etc.); it is part of geology, wider than geology

    expected / accountable

- distribution and migration of elements and isotopes in/on the Earth during Earth evolution - physical chemistry based history

- cycling of elements and isotopes in space and time, its laws (incl. study of biological effects → BIOGEOCHEMISTRY)

- occurrence and distribution of elements and isotopes in the Universe, Sun, Planets, meteorites, and chemistry of Stars, and dust form the interstellar space → COSMO/GEO/CHEMISTRY

Integrating discipline (earth and environmental sciences, planetology)
Introduction:

Geochemist missions:

- determination of relative and absolute amounts of elements, as well as isotope ratios in/on the Earths, its spheres and build up materials (e.g. crust, surface water, troposphere) 
  global database (http://georoc.mpch-mainz.gwdg.de/georoc/; http://earthref.org/GERM/)

- observation and description of distribution and migration of elements and isotopes in/on the Earths, its spheres and build up materials down to minerals/phases

- recognition of distribution and migration laws of elements and isotopes
  overlap mineralogy and petrology
History of geochemistry

Short history, quick development from the 19th century, although
- Lazarus Ercker (II. Rudolf chief inspector of mines): description of ores and their analyses in 1574,
- Swiss Schönbein (discoverer of ozone) introduced the term geochemistry in 1838

- history of discover of elements:
  - in 1789 Lavoisier identified: O, N, H, S, P, C, Cl, F, B, Sb, Ag, As, Bi, Co, Cu, Sn, Fe, Mn, Hg, Mo, Ni, Au, Pt, Pb, W, Zn, Ca, Mg, Ba, Al, Si (used from ancient time, alchemists studied)
  - 1790-1800: U, Zr, Sr, Ti, Y, Be, Cr és Te
  - 1800-1849: Na, K, Nb, Rh, Pd, Ce, Ta, Os, Ir, Li, SE, Cd, I, Br, Th, V, La, Ru, Tb, Er - 46 elements were discovered
History of geochemistry

- development of optical emission spectrograph in 1860 (strong link between analytical chemistry and geochemistry)

- 1860-1900: Rb, In, Cs, Tl, Sc, Ga, Sm, Ho, Tm, Yb, Ge, Pr, Nd, Gd, Dy, He, Ne, Ar, Kr, Xe, Po (Becquerel, 1896), Ra (Curie’s, 1898), Ac
/Mendelejev predicted (1869) eka-Al (Ga), eka-B (Sc), eka-Si (Ge)/

- 1900-1925: the rest: Eu, Lu, Hf, Re

- 1884-1924: analyses of rocks and minerals: F.W. Clarke (USGS, 1908), Data of the Geochemistry (basic dataset; in modern system: native elements, components of atmosphere and hydrosphere, volcanic and plutonic rocks, weathered, sedimentary, metamorphic rocks and ores /5 editions/)
History of geochemistry

- 1904: Geophysical Laboratory (Carnegie Institution of Washington), beginning of experimental petrology, considering of principles of physical chemistry, genesis of rocks and ore deposits

- 1928: Bowen: Evolution of the Igneous Rocks (geochemical differentiation)

- 1952: Brian Mason: Principals of Geochemistry (stability of minerals, thermodynamic, mobility of ions) book
History of geochemistry

- 1911: V.M. Goldschmidt’ doctorate thesis on contact metamorph rocks at Oslo University (using phase rules for minerals assemblages, chemical equilibrium)
  (NEW WAVES: great impact on development of geochemistry)

- 1922-1926: Goldschmidt at Oslo University discovered the significance of structure of minerals (XRD), constrain on distribution of elements in crystallized materials (minerals)

- 1929-1935: Goldschmidt in Göttingen, studying geochemical nature of certain elements, developing quantitative spectrographic analytical method, root of the concept of the geochemical cycles, geochemical evolution of the Earth and the Sun System during geological and pregeological times, replaces of elements, role of trace elements

(Goldschmidt died in 1947 – Geochemistry 1954, Alex Muir)
History of geochemistry

- 1917- significant Russian (‘soviet’) school: V.I. Vernadsky, A.E. Fersmann and A.P. Vinogradov: exploration of mineral resources (communist party controlled research)

- II. World War: previous, during and following WW: study of radioactivity => development of instrument of neutron activation analysis (INAA) => study of isotopes (bases for geochronology) => mass spectrometer (MS) => smaller amount of materials, more accurate and greater number of data

- 1960-1970: plate tectonics => matter cycle (revolution in geochemistry, too), studies and data provided by satellite, space craft, space shuttle, meteorites, lunar rocks => revolution in planetology cosmogeochemistry
**Goldschmidt’s Views on Geochemistry** – Goldschmidt was not shy in his thinking about the importance of geochemistry, as illustrated by a quotation from Geochemistry (Goldschmidt, 1958, edited by Alex Muir following Goldschmidt’s death): “From a human point of view, geochemistry is of the greatest practical importance, especially in its applications to mining, metallurgy, chemical industry, agriculture and, of course, the study of terrestrial materials, particularly the accessible outermost parts of our planet… The results of mineralogy, petrology, and geology form the foundation of geochemistry. Modern atomic chemistry and atomic physics, as well as physical chemistry and chemical physics, give in many cases an essential basis for the understanding of geochemical problems. Geochemistry, however, is not a debtor only in its relations to theoretical chemistry and physics, since modern inorganic crystal chemistry originated from the study of geochemical problems, e.g., the practical use of X-ray spectra for chemical analysis and the development of quantitative optical spectroscopy with the carbon arc.” Goldschmidt was also prescient in his thinking about the linkages among geochemistry, biology, and the environment: “Very close relationships exist between modern geochemistry and pure and applied biology. The circulation and distribution of many chemical elements in nature (are) closely related to biochemical processes in which both plants and animals are involved. Some of the dominant geochemical factors of our time result from the activities of modern man – agriculture, mining, and industry.” We resonate particularly with Alex Muir’s and Goldschmidt’s thoughts on the important connections between observation and theory: “In the general evolution of geochemistry during the last quarter of a century, the most remarkable trend is the tendency not only to accumulate analytical facts, but to find a theoretical explanation of these facts.” (Goldschmidt, 1958).
What is Geochemistry?

- Analytical Geochemistry
- Applied Geochemistry
  - Archaeological Geochemistry
  - Environmental Geochemistry
  - Exploration Geochemistry
  - Medical Geochemistry
  - Urban Geochemistry
- Aquatic Geochemistry
  - Hydrogeochemistry
  - Marine Geochemistry
- Biogeochemistry
- "Classical" Geochemistry
  - Cosmo-Geochemistry
  - Isotope Geochemistry
  - Mantle Geochemistry
  - Ore Geochemistry
  - Organic Geochemistry
  - Sediment Geochemistry
  - Surface Geochemistry
Environmental geochemistry

- **Uranium Stream water**: ICP-MS, detection limit 0.002 µg l⁻¹
  - Number of samples 807
  - Median 0.320 µg l⁻¹

- **Uranium Stream sediment**: XRF, detection limit 1 mg kg⁻¹
  - Number of samples 852
  - Median 2.00 mg kg⁻¹

Maps showing distribution of Uranium (U) in stream water and sediment across Europe.
Environmental geochemistry

“Collage” of the European radon maps published by the national authorities. Colours and levels have not been harmonized in the figure.
Environmental geochemistry

Source:
European Commission, DG Joint Research Centre (JRC),
Institute of Environment and Sustainability, REM group
Environmental geochemistry

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European Commission, DG Joint Research Centre (JRC),
Institute of Environment ans Sustainability, REM Group
The movement of water into a soil depends on land surface slope, vegetation, degree of surface loading, and soil texture, structure, density and compaction. More water moves into the soil zone on natural landscapes compared to urban landscapes with disturbed soils. These schematic drawings compare the generalized disposition and movement of incoming water on a natural plant-covered landscape (A) with that in a disturbed urban landscape (B) with limited vegetation and abundant impervious surfaces.
Urban Geochemistry

As of the late 19th century, a human migration takes places towards urban centers. The population density, and elated activities strain the environment and lead to new problems.

The effect of road traffic has to be quantified to assess ecological strain; examples from Karlsruhe, Baden-Württemberg
Sediment Geochemistry

Tisza River disaster, cyanide spill (2000)

Theiss sampling locations
river kilometers, summer 2000
Environmental geochemistry

environmental geochemistry = geochemistry + environmental science
(surface, low PT, short t)

impact on biosphere

global/regional/local problems → endless, waneless in geochemical cycles, environmental assessment (sampling, methods)
### The stable environmental isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Ratio</th>
<th>% natural abundance</th>
<th>Reference (abundance ratio)</th>
<th>Commonly measured phases</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2H</strong></td>
<td>$^{2}$H/$^{1}$H</td>
<td>0.015</td>
<td>VSMOW (1.5575 $\cdot$ 10$^{-4}$)</td>
<td>$H_2O$, $CH_2O$, $CH_4$, $H_2$, $OH^-$ minerals</td>
</tr>
<tr>
<td><strong>3He</strong></td>
<td>$^{3}$He/$^{4}$He</td>
<td>0.000138</td>
<td>Atmospheric He (1.3 $\cdot$ 10$^{-6}$)</td>
<td>He in water or gas, crustal fluids, basalt</td>
</tr>
<tr>
<td><strong>6Li</strong></td>
<td>$^{6}$Li/$^{7}$Li</td>
<td>7.5</td>
<td>L-SVEC (8.32 $\cdot$ 10$^{-3}$)</td>
<td>Saline waters, rocks</td>
</tr>
<tr>
<td><strong>11B</strong></td>
<td>$^{11}$B/$^{10}$B</td>
<td>80.1</td>
<td>NBS 951 (4.04362)</td>
<td>Saline waters, clays, borate, rocks</td>
</tr>
<tr>
<td><strong>13C</strong></td>
<td>$^{13}$C/$^{12}$C</td>
<td>1.11</td>
<td>VPDB (1.1237 $\cdot$ 10$^{-2}$)</td>
<td>$CO_2$, carbonate, DIC, $CH_4$, organics</td>
</tr>
<tr>
<td><strong>15N</strong></td>
<td>$^{15}$N/$^{14}$N</td>
<td>0.366</td>
<td>AIR $N_2$ (3.677$\cdot$10$^{-3}$)</td>
<td>$N_2$, $NH_4^+$, $NO_3^-$, N-organics</td>
</tr>
<tr>
<td><strong>18O</strong></td>
<td>$^{18}$O/$^{16}$O</td>
<td>0.204</td>
<td>VSMOW (2.0052 $\cdot$ 10$^{-3}$) VPDB (2.0672 $\cdot$ 10$^{-3}$)</td>
<td>$H_2O$, $CH_2O$, $CO_2$, sulphates, $NO_3^-$, carbonates, silicates, C minerals</td>
</tr>
<tr>
<td><strong>34S</strong></td>
<td>$^{34}$S/$^{32}$S</td>
<td>4.21</td>
<td>CDT (4.5005 $\cdot$ 10$^{-2}$)</td>
<td>Sulphates, sulphides, $H_2S$, S-organics</td>
</tr>
<tr>
<td><strong>37Cl</strong></td>
<td>$^{37}$Cl/$^{35}$Cl</td>
<td>24.23</td>
<td>SMOC (0.324)</td>
<td>Saline waters, rocks, evaporites, solvents</td>
</tr>
<tr>
<td><strong>81Br</strong></td>
<td>$^{81}$Br/$^{79}$Br</td>
<td>49.31</td>
<td>SMOB</td>
<td>Developmental for saline waters</td>
</tr>
<tr>
<td><strong>87Sr</strong></td>
<td>$^{87}$Sr/$^{86}$Sr</td>
<td>$^{87}$Sr = 7.0 $^{86}$Sr = 9.86</td>
<td>Absolute ratio measured</td>
<td>Water, carbonates, sulphates, feldspar</td>
</tr>
</tbody>
</table>
## The environmental radioisotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Decay mode</th>
<th>Principal Sources</th>
<th>Commonly measured phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>12.43</td>
<td>$\beta^-$</td>
<td>Cosmogenic, weapons testing</td>
<td>$H_2O$, $CH_2O$</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>5730</td>
<td>$\beta^-$</td>
<td>Cosmogenic, weapons testing, nuclear reactors</td>
<td>DIC, DOC, $CO_2$ $CaCO_3$, $CH_2O$</td>
</tr>
<tr>
<td>$^{36}$Cl</td>
<td>301,000</td>
<td>$\beta^-$</td>
<td>Cosmogenic and subsurface</td>
<td>$Cl^-$, surface $Cl$-salts</td>
</tr>
<tr>
<td>$^{39}$Ar</td>
<td>269</td>
<td>$\beta^-$</td>
<td>Cosmogenic and subsurface</td>
<td>$Ar$</td>
</tr>
<tr>
<td>$^{85}$Kr</td>
<td>10.72</td>
<td>$\beta^-$</td>
<td>Nuclear fuel processing</td>
<td>$Kr$</td>
</tr>
<tr>
<td>$^{81}$Kr</td>
<td>210,000</td>
<td>electron capture</td>
<td>Cosmogenic and subsurface</td>
<td>$Kr$</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>1.6 · 10$^7$ yr</td>
<td>$\beta^-$</td>
<td>Cosmogenic, subsurface, nuclear reactors</td>
<td>$I^-$ and $I$ in organics</td>
</tr>
<tr>
<td>$^{222}$Rn</td>
<td>3.8 days</td>
<td>$\alpha$</td>
<td>Daughter of $^{226}$Ra in $^{238}$U decay series</td>
<td>Rn gas</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>1600</td>
<td>$\alpha$</td>
<td>Daughter of $^{230}$Th in $^{238}$U decay series</td>
<td>$Ra^{2+}$, carbonate, clays</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>75,400</td>
<td>$\alpha$</td>
<td>Daughter of $^{234}$U in $^{238}$U decay series</td>
<td>Carbonate, organics</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>246,000</td>
<td>$\alpha$</td>
<td>Daughter of $^{234}$Pa in $^{238}$U decay series</td>
<td>$UO_2^{2+}$, carbonate, organics</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>4.47·10$^9$</td>
<td>$\alpha$</td>
<td>Primordial</td>
<td>$UO_2^{2+}$, carbonate, organics</td>
</tr>
</tbody>
</table>

$^{10}$Be, $^{26}$Al, $^{32}$Si
Periodicals, Books

Periodicals

- Geochimica et Cosmochimica Acta (GCA)
- Geokhimiya (= Geochemistry International)
- Applied Geochemistry (ApplGeochim)
- Chemical Geology (ChemGeol)
- Aquatic Geochemistry
- Journal of Geochemical Exploration
- Elements

Books:

- Geochemistry (1954) V.M. Goldschmidt
- Geochemistry (1951) K. Rankama & T.G. Sahama
- Handbook of Geochemistry (1969-) K.H. Wedephol
- Geochemistry (1979 ill. 1996) A.H. Brownlow
- Principles of Geochemistry (1982) B. Mason, & C.B. Moore
- Principals of Geochemistry (1997) G. Ottonello
- Principals and Applications of Geochemistry (1998) G. Faure
- Treatise on Geochemistry (2003, 2014) H.D. Holland & K.K. Turekian