Mineralogical and geochemical investigations
Needed information

- The grade of the economic minerals
  - The concentration of a valuable mineral/metal within an ore is often referred to as ore grade
    - The bulk chemical composition
    - The minerals present
    - The proportions of each these and their chemical composition

- Properties that commonly define the workable grade include
  - Grain size distributions
  - Textures and mineral locking patterns
  - Any changes in these features within the deposit
Minerals of interest

- Minerals can be
  - Ore minerals
  - Gangue
    - Without economic value
      - Common rock forming minerals
    - Detrimental (with adverse effects to the beneficiation process)
      - Clay, talc, carbon, baryte
    - Environmentally harmful
      - Hg- and As-minerals
Geochemical classification of elements

- (Goldschmidt classification from Berry & Mason, Elements of Mineralogy)
- Several metals can be chemically bond both silicates and sulphides
- E.g nickel
- Economic cut-off typically
  - 0.5 % in Ni-sulfides
  - 1.5 % in Ni-silicates/carbonates
    - (mainly laterites)


**E.g. Ni ores**

- Typically orthomagmatic origin (Cu-Ni-+/- PGE) ores
  - Largest production from sulfide ores but largest resources in lateritic deposits
  - Associated with mafic and ultramafic igneous rocks
    - Intrusions, particularly layered intrusions
    - Komatitic rocks (lavas, typically Precambrian age)

Sulfide immiscibility is an important ore forming process
- sulfide phase is segregated from the magma and 2) reaches chemical equilibrium with the melt and 3) forms distinctive sulfide-rich layers or magma bodies
- Sulfide ore formation can take place also if mafic magma is intruded into sulfide rich sediments black shales (Norilsk)
Mineralogical challenges in Ni-exploration and mining

Mafic intrusions can contain mafic silicate minerals (olivine, pyroxene) that can have 1-2.5% Ni

- How to distinguish those mafic and ultramafic rocks where sulfide segregation has taken place from those where metals are essentially in silicates?
- How to distinguish Ni anomalies resulting from weathering of Ni-silicates from anomalies induced by Ni-sulfide deposits?
- Once you have discovered a Ni-rich (orthomagmatic) deposit, how to assure that Ni is in the sulfide minerals, not in silicates?
- Since Ni-silicates end up in tailings, what is their environmental impact
## Nickel belt in S-Finland

Geological Survey of Finland, Bulletin 402
FROM GENETIC CONCEPTS TO PRACTICE - LITHOGEOCHEMICAL IDENTIFICATION OF Ni-Cu MINERALISED INTRUSIONS AND LOCALISATION OF THE ORE, PERTTI LAMBERG

<table>
<thead>
<tr>
<th>Factor</th>
<th>Feature to monitor</th>
<th>Lithogeochemical tools applied in Ni exploration</th>
<th>Komatiites</th>
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</thead>
<tbody>
<tr>
<td>Primitive magma</td>
<td>Mg, Ni-rich magma Not PGE-depleted.</td>
<td>-Mg# of olivine, Opx, Cpx</td>
<td>-Ni vs. Cr plot</td>
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<td>-Pd/Cu vs. Pd plot</td>
<td>-Ni, Cr vs. MgO plot</td>
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<td>-Magma type (boninite)</td>
<td>-Incompatible vs. MgO</td>
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<td>-Mg-Fe relationship</td>
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<tr>
<td>Sulphide saturation</td>
<td>Contamination: Anomalous contents of incompatible elements</td>
<td>-HFSE</td>
<td>-REE</td>
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<td></td>
<td></td>
<td>-Zn content of chromite</td>
<td>-Isotopes of Re-Os</td>
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<td></td>
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<td>-Cu/Zr ratio</td>
<td>-Ni-Mg relationship</td>
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<tr>
<td>Sulphide segregation</td>
<td>Chalcophile element, especially PGE, depletion</td>
<td>-Ni vs. Mg# of OI, Opx, Cpx</td>
<td>-Ni vs. MgO of olivine cumulates</td>
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<td></td>
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<td>-Pd/Cu ratio</td>
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<td>-Tl, Eu</td>
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<tr>
<td>Sulphide accumulation</td>
<td>Favourable site for accumulation: feeder zone, bottom parts, depression structures, channelised flows</td>
<td>-MgO</td>
<td>-MgO</td>
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<td>-Presence of olivine ad- and mesocumulates</td>
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<td>-Ni vs. Cr plot</td>
</tr>
</tbody>
</table>
• How to distinguish Ni-anomalies resulting from weathering of Ni-silicates from those of Ni-sulfide mineralizations.
  – In areas with thick weathering zone (e.g. Australia) Ni-contents in weathering zones may not be a good indicator of Ni-sulfide ores (Moon et al. p.80)
• In stead:
  – 1) visual description of weathered rocks
  – 2) relic textures (macro and microscopic)
    • [http://geologicalintroduction.baffl.co.uk/?p=111](http://geologicalintroduction.baffl.co.uk/?p=111)
    • Plus many other examples (of “boxwork texture” and “ore” in the internet)
  – Chemical analyses
    • Ratios of immobile elements e.g. Zr-TiO2-plots (HFSE-plots)
    • **HFSE:s are** small radius compared to their high cationic charge: the z/r ratio.
      – bonding to nearby anions is very strong, that is - they have a high electrical field strength
      – Making HFSE immobile e.g in alteration and weathering reactions
An example:

• Kevitsa: (Cu-)-Ni-PGE ore deposit
  – Main ore body is a disseminated Ni-PGE- sulfide ore. The intrusion has also ultramafic parts, where olivine (Fo 85-87.5 %) contains Ni-up to 1.7 wt%

• Analytical challenge: how to distinguish sulfidic nickel (ore mineral content) from total nickel content?
Other examples

- Possibly co-existing silicates and ore minerals
  - Bauxites: Al-hydroxides and silicates
  - Tin-deposits: casseterite-silicates

- Industrial minerals
  - Carbonate rocks:
  - Carbonates+Ca-Mg-silicates
Geochemistry

• “Geochemistry is the study of the distribution and amounts of the chemical elements in minerals, rocks, soils, water, and the atmosphere, and the study of the circulation of the elements in nature, on the basis of the properties of their atoms and ions.” Goldsmith (1954)

  – In exploration studies, we are not just interested about e.g. Cu or Ni concentration in rocks, but we need to take into account the mineral speciation.
Geochemical analysis

• Geochemical analysis are multi-element analysis
  – a large suite of elements are determined for practical purposes
    • Exploration, environmental analyses etc.
  – level of accuracy varies
  – Aim of the analysis is provide information on the speciation and mineral composition of rocks and soils

• For example *aqua regia* extractions are common, but will only dissolve sulfides, some oxides, and perhaps partially highly altered silicates.
  – Resistant phases like zircon, monazite, sphene, chromite, barite and many other minerals, as well as most silicates, are not dissolved completely.
  – XRF- analyses do not yield information about light elements
Re-evaluation of geochemical data

• Only about 1/1000 mineral discoveries lead to mining!
• Many prospects are recycled
  – They will go through several evaluation cycles over time periods of tens of years
  – Economic value of the deposits may change due to:
• Global markets change
  – Prices of commodities (e.g. increasing demand of base metals)
  – Demand of new commodities (e.g. “IT-metals”)
• New processing methods are developed
  – Previously uneconomical deposits may become economical as new methods are developed
• Analytical methods have developed
  – E.g. development of fast (cost effective) and accurate multi-element geochemical analysis (e.g. Au-exploration and PGEs)
• Economical deposits may exist among deposits previously rendered uneconomical
• The economic analysis of mineral resources (esp. scoping and pre-feasibility stage) will commonly involve re-evaluation/critical review of the old exploration data
  – Geochemistry and mineralogy should be mutually consistent
  – Geophysics, mineralogy and volume estimate should be mutually consistent
  – Trace and minor elements may have been not distinguished due to lack of analysis or improper sampling
  – “Ore potential” (grade, tons, continuity) may have been exaggerated

• A key task of economic geologists is commonly evaluation if the data available justify continuation of the investigations!
Analytical terminology

• A **technique** is any chemical or physical principle we can use to study an analyte.
  – Eg. GFAAS uses both a chemical principle (atomization) and a physical principle (absorption of light).

• A **method** is the application of a technique for a specific analyte in a specific matrix.
  – Water, soil or blood or acid mine drainage

• A **procedure** is a set of written directions telling us how to apply a method to a particular sample,
  – How to obtain samples, handling interferences, and validate results.
  – A method may have several procedures as each analyst or agency adapts it to a specific need.

• A **protocol** is a set of stringent guidelines specifying a procedure that must be followed if an agency is to accept the results. Protocols are common when the result of an analysis supports or defines public policy.
Assaying

• Assays are used to determine as accurately as possible the “true value” of a commodity or commodities in question.

• Specific procedures and methods
  – Commonly a limited range of components/elements analyzed

• Protocols including high number of repeats and certified international reference materials to verify the analytical bias

Assays are also typically higher in cost than (standard) geochemical analyses.
Assaying methods

- Different assaying protocols have been developed
  - Analyses can be purely instrumental (Neutron activation analysis, delayed neutron counting) or produced by chemical treatment such as fusion or acid digestion
  - final analyses commonly by AA, XRF, ICP, ICP/MS, titration or gravimetric methods.
- The concentrations need to match with the optimal a linear dynamic range where the response of the analyte is purely linear.
Assaying laboratories

- Laboratories carrying out assaying need to be accredited/approved.
- The lab/labs being used should have a variety of analytical technologies available.
- Strict QC/QA
- See e.g.
Chemical composition

- Exploration produces information of geochemical composition
  - However, in order to assess the economic and technical feasibility of mining, the contents of commodity minerals and the composition metals in those minerals need to be assessed by appropriate assaying before ore resources can be determined.
- Geochemical data (with wider number of elements) provides however, an important source of information throughout the life of mine.
- If sampling and analysis is too much focused only on few metals of interest, information on trace elements will be lost and the economic value not distinguished
  - E.g. Pampalo gold mine
    - First investigated as Cu-deposit, gold not analyzed
  - Indium in several Zn-ores
Critical considerations needed

• One of the critical issues of the assessment of mineral resources is if the analytical techniques and methods have been appropriate or support the represented conclusions.
• Is there evidence on appropriate level of QA/QC concerning the laboratory protocols and procedures?
• Some knowledge on most common chemical analysis is therefore needed
  – Common laboratory techniques include the following examples
Analytical techniques

• Atomic spectral methods
  – Atomic absorption spectrometry AAS
  – Atomic fluorescence spectrometry AFS
  – Inductively coupled plasma-techniques
    • Optical emission spectrometry ICP-OES
    • Mass spectrometry ICP-MS
  – gamma ray spectrometry
    • Radioactive components
    • NAA
  – X-ray spectrometry
    • XRF
  – Chromatographic methods for anions
AAS atomic absorption spectrometry

• Every element has its own characteristic set of energy levels and thus its own unique set of absorption and emission wavelengths

• In AAS, an external light source (emitting light of a wavelength characteristic of the element of interest) is shone through an atomic vapor obtained by heating the sample until it decomposes to gas.
  – Some of this light is absorbed by the atoms of that element.
  – The amount of light that is absorbed by these atoms is then measured and used to determine the concentration of that element in the sample.
• FAAS (flame AAS),
  • solid samples need to be dissolved.
    – few well-documented interferences
    – samples and standards need not be made very similar. high precision (0.2 to 0.5% relative standard deviation, RSD) determinations, moderate detection limits.

• Graphite furnace AAS a.k.a. Electrothermal ET-AAS.
  – GFAAS high sensitivity and low detection limits, poorer precision
  – matrix interferences without stabilized temperature platform furnace (STPF) technology and Zeeman background correction
ICP OES

• the sample is heated to temperatures high enough to cause not only dissociation into atoms but to cause significant amounts of collisional excitation (and ionization) of the sample atoms to take place.

• Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transitions.

• In OES, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentrations of the elements of interest.
Typical applications of ICP OES

• The major use of ICP-OES in this field is for prospecting purposes.
  – Determinations of major, minor and trace compositions of various rocks, soils, sediments, and related materials.
  – Preparation of geological samples:
    • Commonly lithium metaborate fusion reactions, for materials containing high levels of silica.
    • Acid dissolutions
  • The borate fusion process maintains constant grain size and does not produce orientation effects. The sample thus obtained will be almost perfectly homogenous.
  • Simpler and quicker than dissolution with acid in a microwave pressure vessel. The complete procedure, takes less than 15 minutes using an automated fluxer.
ICP-MS

- Mass spectrometry measures the number of singly charged ions from the elemental species within a sample. Similar to the function of a monochromator.
- A quadrupole mass spectrometer separates the ions of various elements according to their mass-to-charge ratio in atomic mass spectrometry.
Pros of ICP-MS

- Detection limits for most elements equal to or better than those obtained by GFAAS.
- Better through put (smaller lab. samples, faster)
- Both simple and complex matrices with a minimum of matrix interferences (versatile, large number of analysis and elements, reliable)
- Superior detection capability to ICP-OES (AES) with the same sample throughput
- ICP-MS is a fast, multielemental technique and generally has the productivity of ICP-AES, but much lower detection capabilities.
XRF

- A standard method for geological investigations and mining production quality control
- Relatively low cost
- Li-borate fusion for homogenization or pulverized samples
- Fast, moderately low detection limits for metals
  - Bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment
  - Poor detection limits for light elements
    - Bulk chemical analyses of trace elements (in abundances >1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn)
    - in rock and sediment - detection limits for trace elements are typically on the order of a few parts per million
Neutron activation analysis

- Sample is bombarded with neutrons, which induce nuclear reactions—neutron capture and excitation induce gamma-radiation and attenuation of neutrons.
- Source: a nuclear reactor, radioactive source (Americum) or a neutron pulse source (tritium)
- Bulk analysis of composition
  - NAA is mostly used as a reference method for testing alternative methods
  - Industrial mineral analysis (clays, carbonates) in QC/QA of production
  - In-situ analytical method in bore-hole logging!
Mineralogical composition needs to be known for all material that may go through the beneficiation processes.
Grain size

- Fine grained texture may prevent beneficiation
- Cost of grinding
- + more complex processing
- (Craigh Vaughan, Ch 11)

FIGURE 11.1 Differences in grain size reflect the origin and history of a deposit and may affect the comminution and recovery of an ore. (a) Very fine-grained sphalerite and pyrite that are difficult to separate and recover prevented efficient processing of the rich (9% Zn) and large (> 220 million tons) but unmetamorphosed McArthur River Deposit, Australia. (b) Metamorphism recrystallized and coarsened the pyrite, sphalerite, and galena in the ores of the Ruttan Mine, Canada, and permitted easy separation and recovery (width of field = 1,200 µm, the same in both photographs).
Specific power consumption [kWh/sh.ton]

\[ W (\text{specific power consumption}) = 10 \times W_i \left( \frac{1}{\sqrt{P}} - \frac{1}{\sqrt{F}} \right) \]

Product and feed grain sizes (corresponding to 80 % of cumulative curve)

Bond work index

\[ BW' = \frac{44.5}{R^{0.32} \times G^{0.42} \times \left( \frac{10}{\sqrt{P}} + \frac{10}{\sqrt{F}} \right)} \]

Bond work index [kWh/short ton]
Deleterious minerals

- Trace amounts of some “ore mineral” are actually undesirable
  - Particularly arsenic and mercury containing minerals can leave trace amounts of these metals to concentrates inducing penalties
- Phosphorus, calcite are also detrimental to some processes
- Clay minerals, barite e.g. can have adverse effects (clogging) on flotation processes
- Hard minerals such as topaz can also induce significant wear of drilling and grinding equipment
Refractory ores

- Refractory gold
  - Extremely fine-grained gold, completely interlocked into sulfide ore grains (arsenopyrite, pyrhotite)
- Resistant to standard beneficiation procedures
  - cyanide leaching and carbon absorption for Au
- Previously pyrometallurgical roasting required
- Hydrometallurgical processes
  - Autoclave/pressure leaching
  - Bioleaching
- Also refractory PGE-ores exist
  - Pyroxide leaching in autoclave
Mineralogical investigation techniques

• Systematic and adequate sampling of ore as well as the host rock
  – Anything that goes through the mill

• Identification of minerals can be done by
  – Polarized microscope
  – XRD-analysis
    • Identification+ semi quantitative analysis of mineral composition
  – Electron microscopy and ion-probe microanalysis
  – **Electron microscopes**
    • Image analysis
    • Energy dispersive spectrometry
  – Specialized methods: autoradiography, cathodoluminence, differential thermal analysis
Mineral texture

- Grain-size distribution
- Shape of the grains
- Grain boundaries
- Liberation
- Today, quantitative analyses largely produced by automated SEM analyses
  (e.g. MLA)
- Suitable for rock specimen and grinded ore
Modal analyses

• The is basically two ways to assess mineralogical composition:
  – Areal calculations (image interpretation)
  – Point counting
• Scanning electron microscopes with EDS-analysis
• Compositions are today measured automatically by electron microscopes systems (using software like MLA)
• Back calculation of modal compositions increasingly important:
  – QA/QC of resource/reserve estimates from exploration geochemistry/assay data
  – GEOMETALLURGICAL optimization of mining operations
Some examples

- Mineral substitution along grain boundaries and fractures
  - In certain Cr-ores chromite can be substituted by magnetite
  - Weathered sulfide minerals can have goethite rims
  - Cassiterite-stannite ores (\(\text{SnO}_3\cdot\text{Cu}_2\text{FeSnS}_4\))

- Solid solution segregation structures in grains
  - Vanadium-Ti-Fe-Oxide ores (lamelli)
  - Ni-ores (flame-like-pentladite exsolutions in pyrrhotite)

Solid solution metals

- e.g. Hg is a toxic metal and largely unwanted component in ore processing
- can remain as a solid solution in sulfides and induce penalties and environmental impacts