

Day 3

Applications for LA-ICP-MS

- 1-** In situ determination of trace element in minerals on thin sections.
- 2-** Calibration
- 3-** Fluid inclusions
- 4-** Metamorphic minerals
- 5-** Hydrothermal minerals
- 6-** Archaeology
- 7-** Bulk Rock
- 8-** Environmental studies
- 9-** Experimental Petrology
- 10-** Melt inclusions
- 11-** Sulfide
- 12-** Alloy-metal
- 13-** Depth profiling
- 14-** Forensic science
- 15-** Gemology
- 16-** Weathering processes

Introduction

Laser ablation has been applied to the determinations of the trace element concentrations in a wide range of materials such as:

Polymer, Press pellets, Alloy - Metals, Fused glasses, Volcanic glass shards, Melt inclusions, Fluid Inclusion, Leaves, Coral, Wood - Tree ring, Teeth, Biological organism, Shell, Foraminifers, Cannabis, Hair and nails, Fish ears, liquids, ice, frozen soft tissue.

And

minerals such as:

Zircon, Plagioclase, Amphibole, Anthophyllite, Apatite, Monazite, Clinopyroxene, Chromite, Orthopyroxene, Sulphide, Carbonate, Phlogopite, Garnet, Magnetite, Dolomite, Titanite, Uraninite, Spinel, Ilmenite, Rutile, Scheelite, Diamond, Experimental Petrology, Glass, Biotite, Muscovite, Tourmaline, Zeolite.

1- In situ determination of trace element in minerals

Example: We have applied the laser ablation technique in the analysis of the REE in clinopyroxene (cpx) from a komatiite lava flow of Alexo in Canada. Alexo is one of the best preserved komatiite flows in the world. The sample analysed is characterised by well preserved cpx needles in a matrix of chlorite plus 30 µm grains of sphene. Three conclusions could be drawn from these experiments:

1. This configuration allows the acquisition of a signal for as much as one minute using a 30 µm thin section and generates data at the chondritic level. However significant differences in the ablation rate has been observed, dependant on the mineral. For example, ablation of apatite is characterised by the quick removal of at least the 10 first micron within the first seconds of the initiation of the ablation. Once a hole has been drilled, the ablation rate greatly decrease to a normal rate (~ 1 micron/s). To stay on the safe side it would be better to use thicker sections with a 266nm laser and doped the glue used to make the thin section with a single unusual element such as In, in order to monitor the depth of sampling.

2. Comparison between solution-based ICP data and laser ablation-based HR-ICP-MS data demonstrate a better accuracy by laser ablation and shows that the cpx crystallised in equilibrium with a LREE-depleted komatiite lava. Mass balance calculations suggest that as little as 4% of sphene in the mineral separate may explain the LREE enriched pattern of the cpx analysed in solution.

3. The REE budget of well preserved komatiitic sample is stored in small secondary grains of sphene which cast some doubt on the ability of komatiites to fingerprint the geochemistry of the Archaean mantle.

2- Calibration

For fused disk mainly 2 types of standardization has been used: with multiple external standard (e.g. Odegaard), with solution (Pickhard et al, 2000)

The production of fused beads offer improved matrix matching: however a limitation of this methodology is the loss of volatile species as a results of a high fusion temperature. Particle size has an effect on the accuracy and precision of press pellet analyses by laser ablation (Becker et al, 1999). Becker et al have used external standardization using solution and Ni60 and 107Ag as an internal standard. The Relative Sensitivity Factor (RSF) is calculated on diluted multi-element solution. Using certified standard, this technique produced data within ± 20%. Of the certified value

The concentrations are calculated following the equation below:

Concentration (analyte)_{solid} = (intensity (analyte)_{solid} / intensity(internal standard)_{solid}) * (concentration(internal standard)_{solid} / RSF_{solution}) with RSF being the relative sensitivity factor measured on the standard: analyte/internal standard).

List of publications related to calibration of laser ablation analysis:

Bi, M., et al., Study of solution calibration of NIST soil and glass samples by laser ablation inductively coupled plasma mass spectrometry. Applied Spectroscopy, 2000. 54(5): p. 639-644.

Chen, Z., Inter-element fractionation and correction in laser ablation inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry, 1999. 14: p. 1823-1828.

Cousin, H. and B. Magyar, Precision and accuracy of laser ablation-ICP-MS analysis of rare earth elements with external calibration. Mikroch. Acta, 1994. 113: p. 313-323.

Craig, C.A., K.E. Jarvis, and L.J. Clarke, An assessment of calibration strategies for the quantitative and semi-quantitative analysis of calcium carbonate matrices by laser

- ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Journal of Analytical Atomic Spectrometry*, 2000. 15: p. 1001-1008.
- Falk, H.F., et al., Calibration of laser-ablation ICP-MS. Can we use synthetic standards with pneumatic nebulisation? *Fresenius Journal of Analytical Chemistry*, 1998. 362(5): p. 468-472.
- Günther, D., et al., Calibration studies on dried aerosols for laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 1997. 12: p. 165-170.
- Günther, D., et al., Direct liquid ablation: a new calibration strategy for laser ablation-ICP-MS microanalysis of solids and liquids. *Fresenius Journal of Analytical Chemistry*, 1997. 359: p. 390-393.
- Hoffmann, E., C. Lüdle, and H. Scholze, Is laser ablation ICP-MS an alternative to solution analysis of solid samples. *Fresenius Journal of Analytical Chemistry*, 1997. 359: p. 394-398.
- Leach, A.M. and G.M. Hieftje, Methods for shot-to-shot normalization in laser ablation with an inductively coupled plasma time-of-flight mass spectrometer. *Journal of Analytical Atomic Spectrometry*, 2000. 15: p. 1121-1124.
- Motelica-Hieno, M. and O.F.X. Donard, Comparison of UV and IR laser ablation ICP-MS on silicate reference materials and implementation of normalisation factors for quantitative measurements. *Geostandards Newsletter*, 2001. 25: p. 345-359.
- Odegard, M., Preparation of synthetic calibration materials for use in the microanalysis of oxide minerals by direct fusion in high-purity graphite electrodes: preliminary results for quartz and rutile. *Geostandards Newsletter*, 1999. 23: p. 173-186.
- Pickhardt, C., J.S. Becker, and H.J. Dietze, A new strategy of solution calibration in laser ablation inductively coupled plasma mass spectrometry for multi-element trace analysis of geological samples. *Fresenius Journal of Analytical Chemistry*, 2000. 368: p. 173-181.

3- Fluid inclusions

Three main laboratories has conducted some experiments on the ability of laser ablation to measure the concentrations of trace elements in fluid inclusions. In summary, after the pioneer work of Chenery and co-worker from the British geological survey at Nottingham (Shepherd and Chenery 1995; Moissette, et al. 1996) based on a calibration technique involving the encapsulation of microdroplets of standard solution in hydrophobic epoxy resin, Ghazi and co-workers (McCandless, et al. 1997; Ghazi, et al. 1996; Ghazi and Shuttleworth 2000) from the Georgia State University develop a new calibration technique using solutions sealed in microcapillary tubes. More recently Günther and co-workers from ETH develop a quantification procedure using elements concentrations ratios calculated by referencing intensity integrals against signals from external standards (glass and solution) and using Na as an internal standard (Audétat, et al. 1998; Günther, et al. 1997; Günther, et al. 1998, Audétat and Günther 1999; Heinrich et al 1999).

Following the introduction of a paper by Ghazi et al (1997), fluid inclusion are analysed by a variety of non-destructive and destructive techniques. Non destructive methods that have been used successfully for the analysis of major elements in single inclusions include mainly synchrotron X-ray fluorescence (Frantz, et al. 1988; Rankin, et al. 1992; Vanko, et al. 1993). Destructive techniques typically provide greater compositional information on the fluid inclusion and are more widely available than the non destructive techniques. The destructive methods can be divided in two groups:

- Single inclusion analysis method include laser microprobe noble gas mass spectrometry for the analysis of halogens and the noble gases (Irwin and Roedder 1995), ion microprobe analysis of frozen inclusions (Kelly and Burgio 1983; Ayora and Fontarnau 1990; Diamond, et al. 1990), laser ablation atomic emission spectroscopy (Rankin, et al. 1992; Ramsey, et al. 1992; Wilkinson, et al. 1994), and laser ablation inductively coupled plasma mass spectrometry.

- Bulk analysis, crush leaching or decrepitation used for extraction of fluid inclusions (Bottrell, et al. 1988; Channer, et al. 1992; Ghazi, et al. 1993) with different analytical techniques such as gas or ion chromatography, atomic absorption, ICP-ES and ICP-MS (Ghazi, et al. 1993; Banks, et al. 1994).

There are several problems related to the analysis of fluid inclusions by LA-ICP-MS. The main problems are:

- (1) The use of an external and internal standard for quantification purposes. The method used by Chenery and co-workers is based on the use of (i) a dual gas flow system that allowed use of standard solutions and NIST glasses for tuning the instrument, (ii) a high temperature ablation cell which improve the efficiency and reproducibility of fluid release and (iii) a new calibration technique involving the encapsulation of microdroplets of standard solutions in hydrophobic epoxy resins. The method used by Ghazi and co-worker is based on a set of artificial fluid inclusion standard prepared by drawing small volume (0.2-0.3 ml) of standard solution of known concentration into 4 ml volume glass microcapillary tubes . These synthetic external standard are used for the construction of a calibration curve (Cps Vs concentration). More recently Gunther, et al. (1998) and Audéat, et al. (1998) have used a different technique (without a dual gas flow system) in which they integrate the counts, use NIST glasses and solutions in teflon beakers as external standard (Günther, et al. 1997) and Na as an internal standard from microthermometric measurements.
- (2) The size of the inclusion and the ability to calculate the volume of the liquid ablated. The range of volume for fluid inclusion is between 10^{-3} and 10^{-7} ml. Using Ghazi and co-workers method, the volume of solution is perfectly known so that the volume per pulse is known as well. Spikes in element intensities were noted by McCandless et al (1997), Audéat et al (1998) and Shepherd & Chenery (1995), between first bleached fluids versus subsequent analysis, suggesting that accurate element concentration may not be determinate in small fluid inclusion when only one scan is obtained before the fluid is exhausted. In order to increase the acquisition, the sample gas flow has to be reduce once the inclusion is open.
- (3) The presence of solid phases in the inclusions
- (4) Thermal fracturing: Ablation is usually initiated by focussing onto the surface to create a shallow pit hole (2-5 μ m). As the rate of ablation decrease due to beam defocusing, the power is slowly increase whilst continually adjusting the focus to achieve a steady rate of drilling. During this drilling step, an early thermal fracturation may occur which leads to the premature release of the fluid inclusion content (Sheppherd and Chenery 1995). Alternatively an active focussing should keep a constant drilling rate without increasing the power density and potential thermal fracturation.
- (5) Internal vapour pressure of the inclusion: Sheppherd and Chenery (1995) have also noticed that the rate and manner of liquid release are determinate by the volume and internal vapour pressure of the inclusion. A Continuous ablation of the liquid phase within a liquid inclusion is possible at room temperature, but the ablation of a CO₂-rich inclusion lead to an explosive release of the liquid phase. According to Sheppherd and Chenery (1995), for many two phases (liquid + vapour) inclusions, fluid release at room temperature is extended over 1-2 seconds and moreover ablation is often accompanied by the precipitation of salts at the surface, due to capillary attraction of the liquid. High temperature ablation minimise the unpredictable ablation response and the cell temperature used by Sheppherd and Chenery (1995) is always set close to the liquid-vapour homogenisation temperature for the inclusion.
- (6) The high background in Na: Na is a mono isotopic element and its background with our system is around 2×10^6 cps. The contamination source of this high background has also been notice by Sheppherd and Chenery (1995) and remain unknown. It's everywhere !!

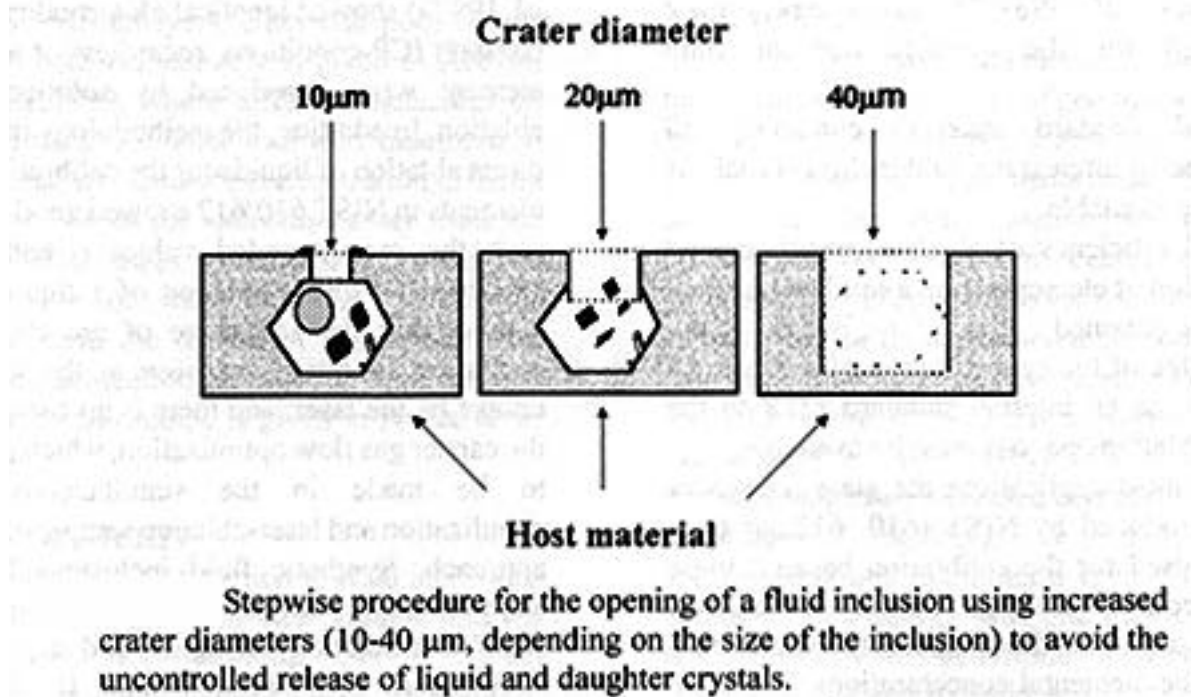


Figure 1-1: Fluid inclusion opening procedure

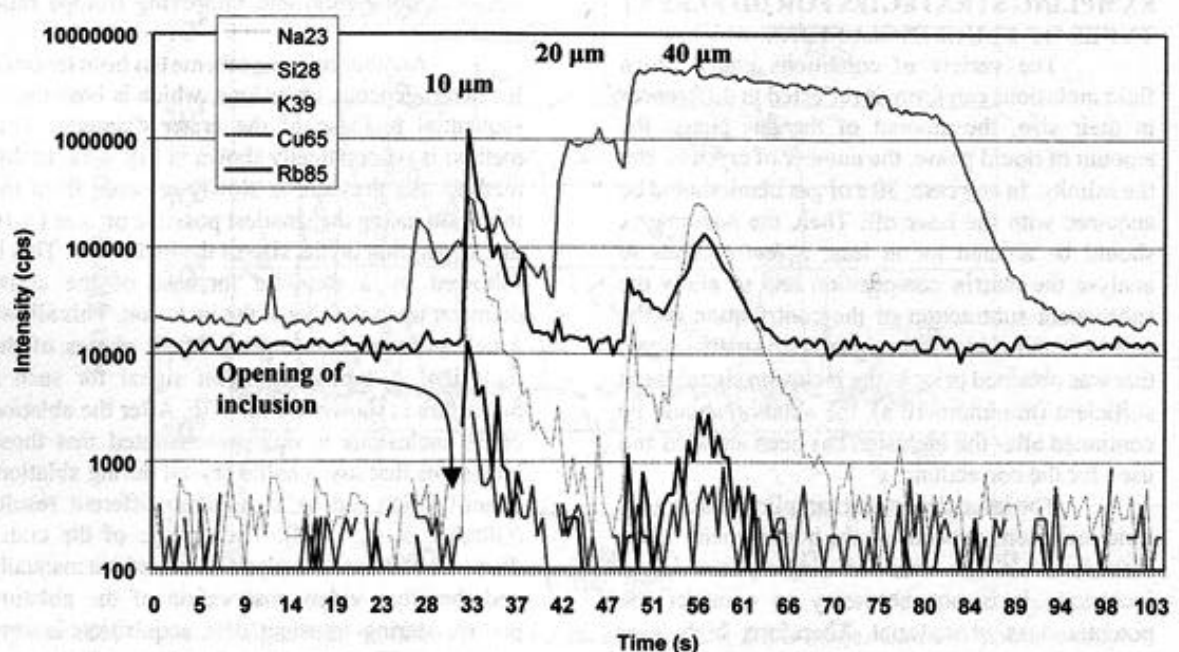


Figure 1-2: Time resolved analysis of a fluid inclusion

4- Metamorphic minerals: Example: garnet

1. Garnet inclusions and geochronological impact:

Metamorphic minerals such as garnet are potential hosts for accessory phases such as monazite, xenotime or zircon, which control the Hf and Rare Earth Element (REE) budget of the host rock. An understanding of the trace element distribution is therefore crucial for the interpretation of bulk Nd and Hf isotopic composition used for a geochronological purpose. Figure 1-4 shows the time-resolved analyses of a garnet displayed in the GLITTER™ program after automatic export from the ELEMENT2 data acquisition software. After an initial gas blank measurement, the garnet is ablated. The area marked A displays the intensity of all element analyses versus time. Area B shows the variation of ^{29}Si in counts per second versus time. The brightness of the colors in Area A is proportional to the elemental signal intensity. From this plot, an inclusion can be detected half way during the ablation. Figure 1-5 shows the REE pattern from this inclusion, normalized to chondrite, and emphasizes the applicability of time resolved analysis software tools such as Glitter™, to depict such inclusions.

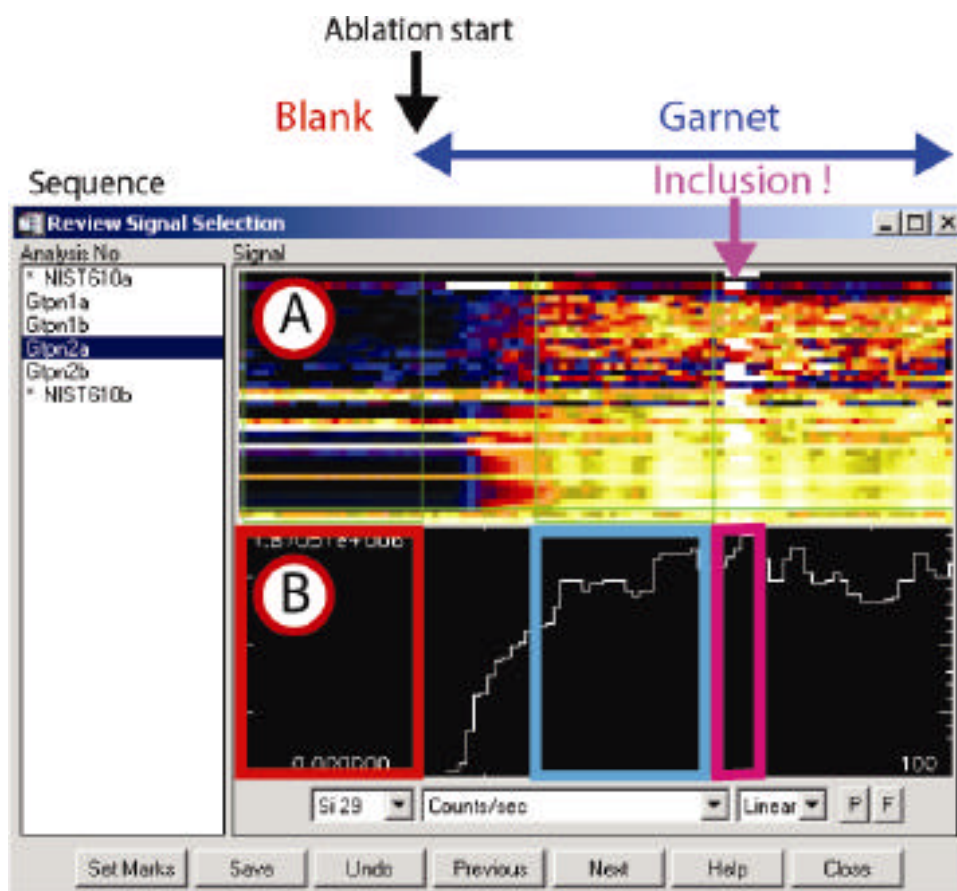


Figure 1-4: Time resolved analysis of a garnet

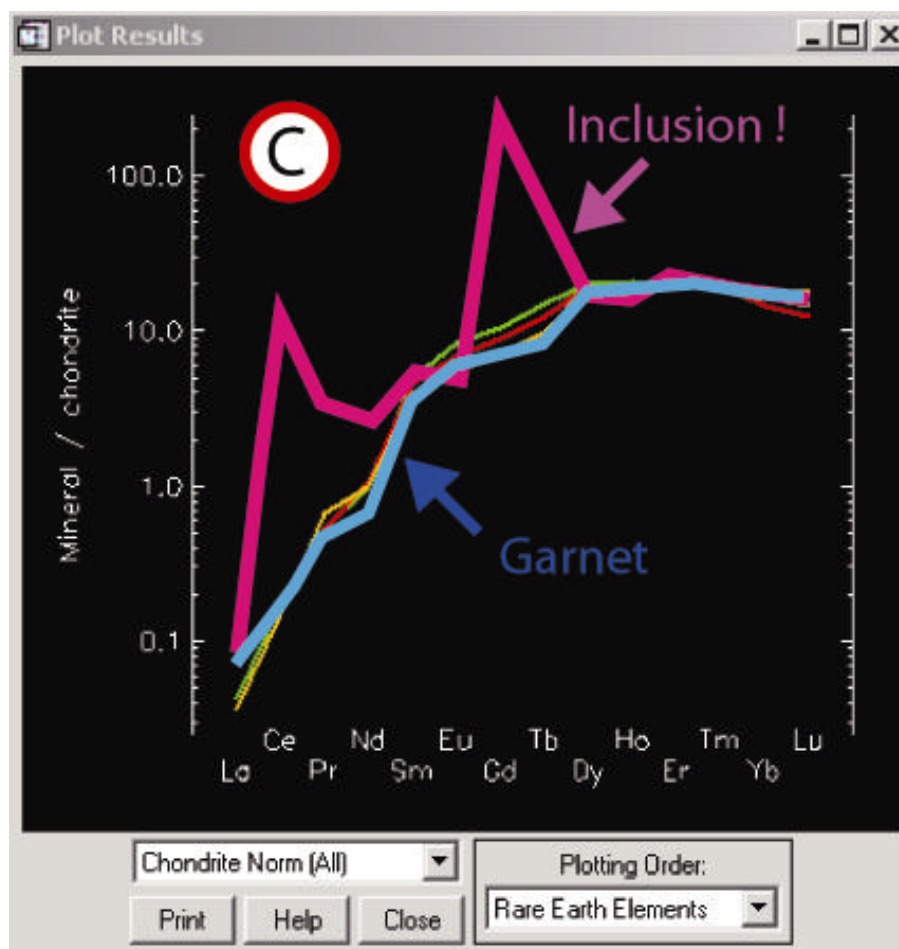


Figure 1-5: Chondrite normalized REE pattern across the same garnet

2. Garnet thermo-geobarometry (Kosler, GAC MAC course):

-Y in garnet. The Y budget is control by the xenotime in pelitic rocks. The Y content of garnet that grew in equilibrium with xenotime is a function of the temperature. This thermometer works well at 450-500 C (garnet and staurolite stability field):

$$\ln(Y \text{ in Gt in ppm}) = ((16031 \pm 862)/T) - (13.25 \pm 1.12)$$

-Ni in garnet: the partition of Ni between olivine and garnet is dependant on the temperature, especially for High Pressure and Ultra High Pressure rocks:

$$T(C) = (1000 / (1.506 - 0.186(\ln(\text{Ni content of Gt in ppm}))))$$

And

$$\ln_{Ni}^{Gt/Ol} = \frac{T}{8772} + 2.53$$

(6) The REE distribution within the garnet could also provide valuable information on the metamorphic gradient. An accurate determination of the heavy REE and Eu anomaly provides a reliable estimate of the pressure (therefore acting as a geobarometer):

$$P(\text{kbar}) = 3.6 + 5.6(\text{Gd/Dy})^{\text{Gt}}$$

3. Diffusion rates in garnet as a metamorphic history tracer

Due to the slow diffusion rate of trace elements in garnet, a comparison with the distribution of the major elements, REE, Y or Mn has been used to monitor the garnet reaction history. Following the arrhenius equation, the diffusion coefficient is pressure and temperature dependant but in metamorphic rock, temperature is the main limiting factor in diffusion.

$$D = D_0 * e \times p \frac{-E_a + P V}{RT}$$

D0 = diffusion rate at infinite high temperature

Ea = activation energy

R = gas constant

T = temperature

-V = volume change

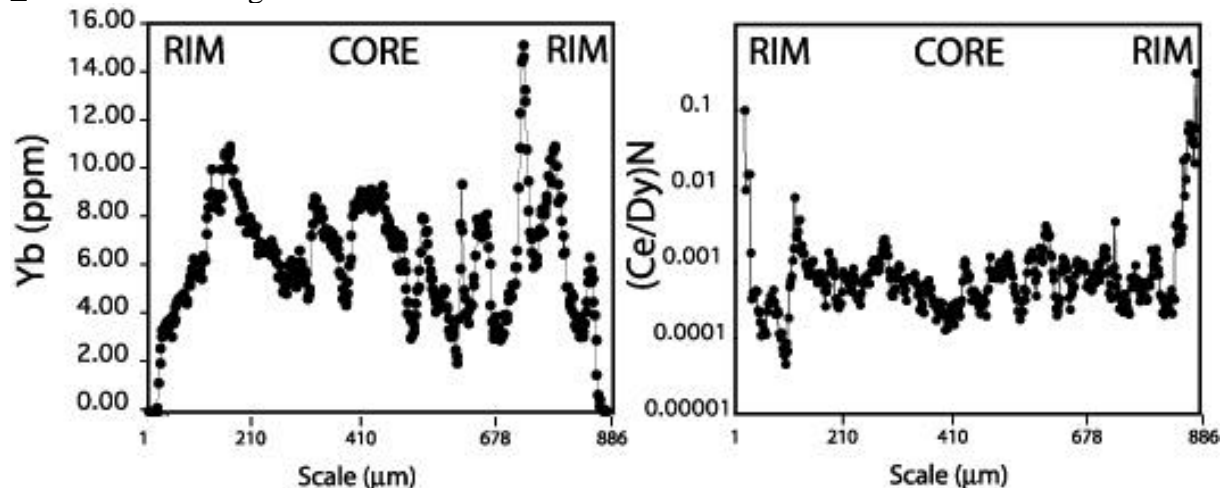


Figure 1-6: Variation of Yb and the light REE fractionation (Ce/Dy) within a garnet

Core-rim trace element variation is temperature dependant and could therefore provide valuable information on the metamorphic history of the host rock. The figure above shows the variations of Yb and the light REE fractionation (Ce/Dy) within a garnet. This figure is the result of a continuous ablation along a line moving from one rim of the garnet grain to the other. It shows a clear depletion in heavy REE along the rims of the garnet, which might be related to a diffusion process.

5- Hydrothermal minerals: example: scheelite

Scheelite is a widespread accessory mineral in hydrothermal gold deposits, and its rare earth element (REE) patterns and Nd and Sr isotopic compositions can be used to constrain the path and origin of the mineralising fluids and the age of the hydrothermal activity.

Due to their similar electronic configuration, the rare-earth elements (REE) have similar chemical properties and behave coherently during geochemical processes. Fractionation between REE is mainly a consequence of two of their chemical properties: (i) They are very electropositive and occur in nature as trivalent cations, whose ionic radii decrease slightly from La to Lu. The resulting fractionation is a smooth function of the atomic number. (ii) Eu and Ce occur as Eu^{2+} and Ce^{4+} under certain redox conditions, and their chemical properties then differ from those of trivalent REE. Consequently, the REE are effective indicators of geochemical processes involving trace element partitioning between minerals or between mineral and melt/fluid. The REE patterns of hydrothermal minerals have been used to constrain the sources of the ore-forming fluids, the physical and chemical properties of fluids during dissolution/transport, the dynamics of hydrothermal systems, the mechanisms of crystal growth, or the genetic type of deposits and the nature of ore-forming fluids. Previous studies have revealed two contrasted REE patterns for scheelite

associated with gold (Sylvester and Ghaderi 1997; Ghaderi et al. 1999); a middle REE (MREE)-enriched pattern with a small positive Eu-anomaly (type I), and a flat pattern with a high positive Eu-anomaly (type II).

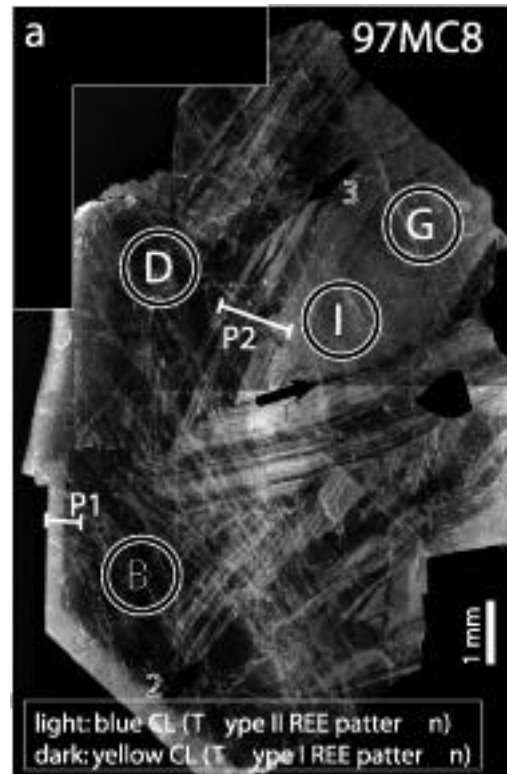


Figure 1-7: Cathodoluminescence image of a scheelite grain

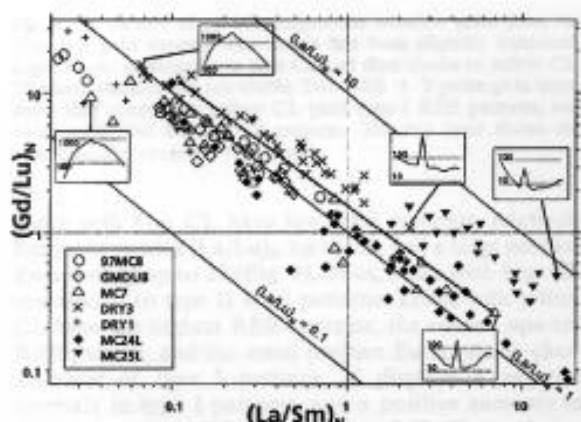


Figure 1-8: Micrometric zonation: La/Sm Vs. Gd/Lu ratio normalised to the chondrite variations within a single scheelite grain.

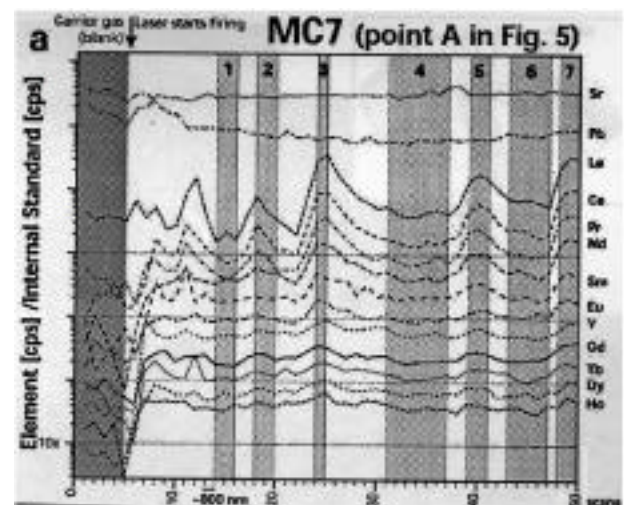


Figure 1-9: Nanometric zonation: intra-sector zoning within the scheelite

Intra-sectorial growth discontinuities, syn-crystallisation brittle deformation, and variations in the relative growth velocities of crystallographically equivalent faces suggest a complex crystallisation history under dynamic hydraulic conditions. The

co-existence of MREE-enriched and MREE-depleted patterns within single scheelite crystals can be explained by the precipitation of a scheelite, which strongly partitions MREE relative to light and heavy REE.

6- Archaeology

Rocks

Blet, M., D. Binder, and B. Gratuze, Essais de caractérisation des solex Bédouliens provençaux par analyse chimique élémentaire. *Revue d'Archéométrie*, 2000. 24: p. 149-167.

Artefacts:

Glass

De Raedt, I., et al., Trace analysis for distinguishing between Venetian and facon-de-Venise glass vessels of the 16th and 17th century. *Journal of Analytical Atomic Spectrometry*, 2001. 16: p. 1012-1017.

Objects

Devos, W., C. Moor, and P. Lienemann, Determination of impurities in antique silver objects for authentication by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Journal of Analytical Atomic Spectrometry*, 1999. 14: p. 621-626.

Watling, R.J., et al., Gold fingerprinting by laser ablation inductively coupled mass spectrometry. *Spectrochimica Acta*, 1994. 49B: p. 205-291.

Coins:

Gondonneau, A., M.F. Guerra, and J.-N. Barrandon, Sur les traces de l'or monnayé: recherche de provenances par LA-ICP-MS. *Revue d'archéométrie*, 1996. 20: p. 23-32.

Gratuze, B., M. Blet-Lemarquand, and J.N. Barrandon, Mass spectrometry with laser sampling: A new tool to characterize archaeological materials. *Journal of Radioanalytical & Nuclear Chemistry*, 2001. 247: p. 645-656.

Junk, S.A., Ancient artefacts and modern analytical techniques - Usefulness of laser ablation ICP-MS demonstrated with ancient gold coins. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials & Atoms*, 2001. 181: p. 723-727.

7- Bulk Rock Analysis

The main disadvantages of solution analyses are the incomplete dissolution of refractory phases and the precipitation of some element in weak acid before the measurement. The production of fused beads offer improved matrix matching; however a limitation of this methodology is the loss of volatile species as a result of a high fusion temperature. Particle size has an effect on the accuracy and precision of press pellet analyses by laser ablation. Backer et al have used external standardization using solution and Ni60 and 107Ag as an internal standard. The Relative Sensitivity Factor (RSF) is calculated on diluted multielement solution. Using certified standard, this technique produce data within $\pm 20\%$. Of the certified value The concentrations are calculated following the equation below:

Concentration (analyte)_{solid} = (intensity (analyte)_{solid} / intensity(internal standard)_{solid}) * (concentration(internal standard)_{solid} / RSF_{solution}) with RSF being the relative sensitivity factor measured on the standard: analyte/internal standard)

Ni Sulphide Fire assay:

Guo, X. and F.E. Lichte, Analysis of rocks, soils and sediments for the chalcophile elements by laser ablation-inductively coupled plasma mass spectrometry. *Analyst*, 1995. 120: p. 2707-2711.

Use of Fire assay technique to produce a Nickel sulphide mini bead that will be later on ablated to measure the concentrations of chalcophile elements in various rocks. The heterogeneity within the bead is compensated with a large sample area (10% of the whole bead). The recovery as well is a factor of error and is higher than 95%. The limit

of detection for the chalcophile elements are between 1-100 ppb. The main disadvantage of solution analyze is the precipitation of elements such as As and Sb in aqua regia as well as the interferences of Cu and Zn polyatomic species on Ru, Rh and Pd.

(Becker and Dietze 1999)

XRF disk

Laser ablation could be a complementary technique for XRF. The advantages are the ability to dissolve refractory minerals and analyze accurately elements such as Zr or Nb in soils for example. Different technique of quantification has been used. External standardization require the previous analyze by RXF to provide an internal standard (Odegard). More recently, Günther et al have tested the use of Li from the flux as an internal standard. However this quantification technique require the precise measurement of the lithium content of each batch of Li flux before. This measurement is performed using known external standards. This technique could provide reproducibility better than 10% for concentrations above 1ppm and better than 15% for lower concentration (Günther et al). Other claim a better accuracy, about 5% with external/internal standardization (Lichte). Limit of detection depends on the dilution factor 1/5-1/7) The melting point of Li metaborate is about 845C and Li tetraborate about 920C.

Perkins, W.T., N.J.G. Pearce, and T.E. Jeffries, Laser ablation inductively coupled plasma mass spectrometry: a new technique for the determination of trace and ultra-trace elements in silicates. *Geochimica et Cosmochimica Acta*, 1993. 57: p. 475-482.

Günther, D., et al., Elemental analyses using laser ablation-inductively coupled mass spectrometry (LA-ICP-MS) of geological samples fused with Li₂B₄O₇ and calibrated without matrix-matched standards. *Mikrochim. Acta*, 2001. 136: p. 101-107.

Lichte, F.E., Determination of elemental content of rocks by laser ablation inductively coupled plasma mass spectrometry. *Analytical Chemistry*, 1995. 67: p. 2479-2485.

Ødegård, M. and M. Hamester, Preliminary investigation into the use of a high resolution inductively coupled plasma mass spectrometer with laser ablation for bulk analysis of geological materials fused with Li₂B₄O₇. *Geostandard Newsletter*, 1997. 21: p. 245-252.

Ødegård, M., et al., Application of a double-focussing magnetic sector inductively coupled plasma mass spectrometer with laser ablation for the bulk analysis of rare earth elements in rocks fused with Li₂B₄O₇. *Fresenius Journal of Analytical Chemistry*, 1998. 362(5): p. 477-482.

Becker, J. S. and H.-J. Dietze (1999). "Determination of trace elements in geological samples by ablation inductively coupled plasma mass spectrometry." *Fresenius Journal of Analytical Chemistry* **365**: 429-434.

Press Pellets

Analyses of press pellets represent the earliest work done with laser ablation. This work highlight the use of an internal standard in order to compensate for difference in ablation yield.

Gray, A.L., Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry. *Analyst*, 1985. 110: p. 551-556.

Imai, N., Quantitative analysis of original and powdered rocks and mineral inclusions by laser ablation inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, 1990. 235(2): p. 381-391.

Klemm, W. and G. Bombach, A simple method of target preparation for the bulk analysis of powder samples by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Fresenius Journal of Analytical Chemistry*, 2001. 370: p. 641-646.

Raith, A. and R.C. Hutton, Quantification methods using laser ablation ICP-MS . Part 1: Analysis of powders. *Fresenius Journal of Analytical Chemistry*, 1994. 350((4-5)): p. 242-246.

Raith, A., R.C. Hutton, and J. Godfrey, Quantitation methods using laser ablation ICP-MS . Part 2: Evaluation of new glass standards. *Fresenius Journal of Analytical Chemistry*, 1996. 354: p. 163-168.

Tao, G.H., et al., Determination of mercury in sediment samples by laser ablation inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.*, 2002. 17: p. 560-562. (the sedimentary samples are pressed to a pellet. A certified sample is prepared the same way and used as an external standard. No internal standard were used for the quantification and good reproducibility were observed)

Free Flux melting:

(Use of Ir strip heating device to melt samples such as basalt but heterogeneity problems. Need to mix the sample with Mg for example and chill the sample very rapidly)

Reid, J.E., et al., Determination of Zr and Hf in a flux-free fusion of whole rock samples using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) with isotope dilution calibration. *Geostandards Newsletter*, 1999. 23: p. 149-155. (Use of an iridium strip heating system with isotopic dilution. The powder is dry down with the spike, then melted for 2 mn at 1600C, then regrinded and remelted. The precision were better than 1% for Zr and about 3,5% for Hf)

Fedorowich, J.S., et al., A rapid method for REE and trace-element analysis using laser sampling ICP-MS on direct fusion whole-rock glasses. *Chemical Geology*, 1993. 106(3-4): p. 229-249. (Use of a W heating strip. optimisation of the system was observed for sample with less than 25mg at 1800C for 2mn. Precision were between 5-15% on 5 replicates)

Norman, M.D., et al., Quantitative analysis of trace elements in geological materials by laser ablation ICPMS: instrumental operation conditions and calibration values of NIST glasses. *Geostandards Newsletter*, 1996. 20: p. 247-261. (use of Ir strip heating to melt some USGS standard, however incomplete dissolution has been observed for 2 doleritic samples (W2 and DNC1))

8- Environmental Studies

Laser ablation ICP-MS is more and more widely used in plants and animals with incremental structure such as tree rings and incremental growth of mollusk, shell, bones, teeth, fish otoliths. More recently, particule trapped by filter used to monitor pollution in industrial area has been ablated (or more exactly re-volatilise) for their trace element and Pb isotopic composition to trace the source of pollution.

Shells and otoliths are by far the most widely used with LA-ICP-MS since they potentially can provide information on the timing of exposition to a specific pollutant (monitor changes in their environment from seawater to river influences) and can record past movements of the species. Those species can also store their information inside the sediments for longer periods, as long as the diagnosis doesn't obscure this primary information. Usually the outer part of the otolith is most likely to record the environmental changes. By opposition with the soft tissue, the incremental growth of the shells can monitor pollution peaks in elements such as Pb, Cd, Cu and Zn.

The study of corals is another growing field of research and recent studies have demonstrated that elements such as B, Mg, Mn, Sr and U show seasonal variations which could be used as paleothermometers. Ratios such as Sr/Ca, Mg/Ca are potential good indicators of environmental changes. Studies have also shown that these paleothermometry properties are species and latitude dependent and that trace elements such as Ba could also be influenced by local planktonic blooms.

Once again the lack of proper standard is a problem and the usual NIST standard is not suitable. In order to use a geochemical match to the coral Sinclair et al (1998) have produced a wollastonite glass from coral. However this standard is not a real match.

Other studies have focussed on the trace element uptake of plants by monitoring those trace elements in leaves, ribs and tree rings using C13 as an internal standard and doped cellulose made external standard.

Hofmann et al has also monitored the long term diffusion of mercury in teeth, due to amalgam. Other research focuses on the trace element variations in ice core using a frozen sample cell.

Alteyrac, J., et al., Mise au point d'une méthode de dosage des éléments minéraux du bois de chêne par ablation laser ICP-MS. *Analyst*, 1995. 23: p. 523-526.

Cave, M.R., et al., Environmental analysis [Review]. *Journal of Analytical Atomic Spectrometry*, 2000. 15: p. 181-235.

- Chin, C.-J., C.-F. Wang, and S.-L. Jeng, Multi-element analysis of airborne particulate matter collected on PTFE-membrane filters by laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 1999. 14: p. 663-668.
- Cox, A., et al., Trace element profiling of dental tissues using laser ablation inductively coupled plasma mass spectrometry. *Fresenius Journal of Analytical Chemistry*, 1996. 354: p. 254-258.
- Durrant, S.F. and N.I. Ward, Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) for the multielemental analysis of biological materials: a feasibility study. *Food chemistry*, 1994. 49: p. 317-323.
- Evans, R.D., P. Richner, and P.M. Outridge, Micro-spatial variations of heavy metals in the teeth of Walrus as determined by laser ablation ICP-MS: the potential for reconstructing a history of metal exposure. *Archives of Environmental Contamination & Toxicology*, 1995. 28.
- Fallon, S.J., et al., Corals at their latitudinal limits: laser ablation trace element systematic in *Porites* from Shirigai Bay, Japan. *Earth and Planetary Science Letters*, 1999. 172: p. 221-238.
- Fallon, S.J., J.C. White, and M.T. McCulloch, *Porites* corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea. *Geochimica et Cosmochimica Acta*, 2002. 66: p. 45-62.
- Fuge, R., et al., Minor and trace element chemistry of modern shells: a laser ablation inductively coupled plasma mass spectrometry study. *Applied Geochemistry*, 1993. 2: p. 111-116.
- Garbe-Schönberg, C.-D., C. Reimann, and V.A. Pavlov, Laser ablation ICP-MS analyses of tree-ring profiles in pine and birch from N Norway and NW Russia - a reliable record of the pollution history of the area. *Environmental Geology*, 1997. 32: p. 9-16.
- Gemperline, P.J., R.A. Rulifson, and L. Paramore, Multi-way analysis of trace elements in fish otoliths to track migratory patterns. *Chemometrics & Intelligent Laboratory Systems*, 2001. 60: p. 135-146.
- Ghazi, A.M., et al., New applications for laser ablation high resolution ICPMS (LA-HR-ICP-MS): Quantitative measurements of gallium diffusion across human root dentin. *Journal of Analytical Atomic Spectrometry*, 2000. 15: p. 1335-1341.
- Ghazi, A.M., et al., Nanoleakage at the dentin adhesive interface: a new application for laser ablation-sector field-ICPMS. *Journal of Analytical Atomic Spectrometry*, 2002. 17: p. 682-687.
- Hlawatsch, S., et al., Trace metal fluxes to ferromanganese nodules from the western Baltic Sea as a record for long-term environmental changes. *Chemical Geology*, 2002. 182: p. 697-709.
- Hoffmann, E., et al., Analytical investigations of tree rings by laser ablation ICP-MS. *Fresenius Journal of Analytical Chemistry*, 1994. 350: p. 253-259.
- Hoffmann, E., C. Ludke, and H. Stephanowitz, Application of laser-ICP-MS in environmental analysis. *Fresenius Journal of Analytical Chemistry*, 1996. 355: p. 900-903.
- Hoffmann, E., H. Stephanowitz, and J. Skole, investigations of the migration of elements in tree rings by laser-ICP-MS. *Fresenius Journal of Analytical Chemistry*, 1996. 355: p. 690-693.
- Hoffmann, E., et al., Investigation of mercury migration in human teeth using spatially resolved analysis by laser ablation-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 2000. 15(6): p. 663-667.
- Hoffmann, E., et al., Spatial determination of elements in green leaves of oak trees (*Quercus robur*) by laser ablation-ICP-MS. *Fresenius Journal of Analytical Chemistry*, 2000. 367: p. 579-585.
- Imai, N. and K. Shimokawa, ESR ages and trace element in a fossil mollusc shell. *Applied Radiation and isotopes*, 1993. 44: p. 161-165.
- Lazareth, C.E., et al., Sclerosponges as a new potential recorder of environmental changes: Lead in *Ceratoporella nicholsoni*. *Geology*, 2000. 28(6): p. 515-518.
- Lea, D.W. and P.A. Martin, A rapid mass spectrometric method for the simultaneous analysis of barium, cadmium and strontium in foraminifera shells. *Geochimica et Cosmochimica Acta*, 1996. 60: p. 3143-3149.
- Lee, K.M., et al., Use of laser ablation inductively coupled plasma mass spectrometry to provide element versus time profiles in teeth. *Analytica Chimica Acta*, 1999. 395: p. 179-185.

- Ma, R., et al., Assessment of airborne platinum contamination via ICP-mass spectrometric analysis of tree bark. *Journal of Analytical Atomic Spectrometry*, 2001. 16: p. 1070-1075.
- Outridge, P.M. and R.D. Evans, Effect of laser parameters and tooth type on the ablation of trace metals from mammalian teeth. *Journal of Analytical Atomic Spectrometry*, 1995. 10: p. 595-600.
- Price, G.D. and N.J.G. Pearce, Biomonitoring of pollution by cerastoderma edule from the British Isles: a laser ablation ICP-MS study. *Marine pollution bulletin*, 1997. 34: p. 1025-1031.
- Prohaska, T., et al., INVESTIGATION OF ELEMENT VARIABILITY IN TREE RINGS OF YOUNG NORWAY SPRUCE BY LASER-ABLATION-ICPMS. *Science of the Total Environment*, 1998. 219: p. 29-39.
- Raith, A., et al., Environmental monitoring on shellfish using UV laser ablation ICP-MS. *Fresenius Journal of Analytical Chemistry*, 1996. 355: p. 789-792.
- Rauch, S., M. Lu, and G.M. Morrison, Heterogeneity of platinum group metals in airborne particles. *Environmental Science & Technology*, 2001. 35: p. 595-599.
- Rauch, S., G.M. Morrison, and M. Moldovan, Scanning laser ablation-ICP-MS tracking of platinum group elements in urban particles. *Science of the Total Environment*, 2002. 286: p. 243-251.
- Richardson, C.A., S.R.N. Chenery, and J.M. Cook, Assessing the history of trace metal (Cu, Zn,Pb) contamination in the North Sea through laser ablation ICP-MS of horse mussel *Modiolus modiolus* shells. *Marine Ecology-Progress Series*, 2001. 211: p. 157-167.
- Roberts, M.S., et al., Trace element variations in coeval holocene speleothems from GB cave, southwest England. *Holocene*, 1999. 9: p. 707-713.
- Schettler, G. and N.J.G. Pearce, Metal pollution recorded in extinct *Dreissena Polymorpha* communities, lake Breitling, Havel lakes system, Germany - A laser ablation inductively coupled plasma mass spectrometry study. *Hydrobiologia*, 1996. 37: p. 1-11.
- Scholze, H., et al., Analysis of leaves by using the laser ICP-MS with isotope dissolution method. *Fresenius Journal of Analytical Chemistry*, 1996. 355: p. 892-894.
- Sinclair, D.J. and M.T. McCulloch, The coral record of terrestrial fluxes into the Great Barrier Reef: Analysis of trace elements in inshore corals by laser-ablation ICP-MS. *RSES - Annual report*, 1997: p. 138-139.
- Sinclair, D.J., L.P.J. Kinsley, and M.T. McCulloch, High resolution analysis of trace elements in corals by laser ablation ICP-MS. *Geochimica et Cosmochimica Acta*, 1998. 62: p. 1889-1901.
- Stoll, H.M., Y. Rosenthal, and P. Falkowski, Climate proxies from Sr/Ca of coccolith calcite: calibration from continuous culture of *Emiliana huxleyi*. *Geochimica et Cosmochimica Acta*, 2002. 66: p. 927-936.
- Tanaka, S., et al., Rapid and simultaneous multi-element analysis of atmospheric particulate matter using inductively coupled plasma mass spectrometry with laser ablation sample introduction. *Journal of Analytical Atomic Spectrometry*, 1998. 13: p. 135-140.
- Toland, H., et al., A study of sclerochronology by laser ablation ICP-MS. *Journal of Analytical Atomic Spectrometry*, 2000. 15: p. 1143-1148.
- Vander Putten, E., et al., High resolution distribution of trace elements in the calcite shell layer of modern *Mytilus edulis*: Environmental and biological controls. *Geochimica et Cosmochimica Acta*, 2000. 64: p. 997-1011.
- Watmough, S.A., T.C. Hutchinson, and R.D. Evans, Application of laser ablation inductively coupled plasma-mass spectrometry in dendrochemical analysis. *Environmental Science & Technology*, 1997: p. 114-118.
- Watmough, S.A., T.C. Hutchinson, and R.D. Evans, Development of solid calibration standards for trace elemental analyses of tree rings by laser ablation inductively coupled plasma-mass spectrometry. *Environmental Science & Technology*, 1998. 32(14): p. 2185-2190.
- Watmough, S.A., T.C. Hutchinson, and R.D. Evans, The quantitative analysis of sugar maple tree rings by laser ablation in conjunction with ICP-MS. *Journal of Environmental Quality*, 1998. 27(5): p. 1087-1094.
- Wu, G. and C. Hillaire-Marcel, Application of LP-ICP-MS to benthic foraminifers. *Geochimica et Cosmochimica Acta*, 1995. 59: p. 409-414.

9- Experimental Petrology (partition coefficient)

- Adam, J. and T. Green, Experimentally determined partition coefficients for minor and trace elements in peridotite minerals and carbonatitic melt, and their relevance to natural carbonatites. *European Journal of Mineralogy*, 2001. 13: p. 815-827.
- Bea, F., M.D. Pereira, and A. Stroh, Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation-ICP-MS study). *Chemical Geology*, 1994. 117: p. 291-312.
- Bea, F., et al., Pressure-dependence of rare earth element distribution in amphibolite- and granulite- grade garnets. A LA-ICP-MS study. *Geostandard Newsletter*, 1997. 21: p. 253-270.
- Dalpé, C. and D.R. Baker, Partition coefficients for rare-earth elements between calcite amphibole and Ti-rich basanitic glass at 1.5 Gpa, 110°C. *Mineral Magazine*, 1994. 58A: p. 207-208.
- Dalpé, C., D.R. Baker, and S.R. Sutton, Synchrotron X-ray-fluorescence and laser-ablation ICP-MS microprobes: useful instruments for analysis of experimental run-products. *Canadian Mineralogist*, 1995. 33: p. 481-498.
- Ertel, W., et al., The solubility of rhenium in silicate melts: Implications for the geochemical properties of rhenium at high temperatures. *Geochimica et Cosmochimica Acta*, 2001. 65: p. 2161-2170.
- Foley, S.F., et al., Trace element partition coefficients for clinopyroxene and phlogopite in an alkaline lamprophyre from Newfoundland by LAM-ICP-MS. *Geochimica et Cosmochimica Acta*, 1996. 60: p. 629-638.
- Foley, S.F., M.G. Barth, and G.A. Jenner, Rutile/melt partition coefficients for trace elements and an assessment of the influence of rutile on the trace element characteristics of subduction zone magmas. *Geochimica et Cosmochimica Acta*, 2000. 64: p. 933-938.
- Horn, I., et al., Experimentally determined partitioning of high field strength- and selected transition elements between spinel and basaltic melt. *Chemical Geology*, 1994. 117: p. 193-218.
- Jenner, G.A., et al., Determination of partition coefficient for trace elements in high pressure-temperature experimental run products by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS). *Geochimica et Cosmochimica Acta*, 1993. 58: p. 5099-5103.
- Klemme, S., et al., Experimentally determined trace and minor element partitioning between clinopyroxene and carbonatite melt under upper mantle conditions. *Earth and Planetary Science Letters*, 1995. 133(3-4): p. 439-448.
- Sattari, P., et al., Experimental constraints on the sulfide- and chromite-silicate melt partitioning behavior of rhenium and platinum-group elements. *Economic Geology & the Bulletin of the Society of Economic Geologists*, 2002. 97: p. 385-398.
- Thompson, G.M. and J. Malpas, Mineral/melt partition coefficients of oceanic alkali basalts determined on natural samples using laser ablation-inductively coupled plasma-mass spectrometry (LAM-ICP-MS). *Mineralogical Magazine*, 2000. 64: p. 85-94.
- Veksler, I.V., et al., Trace element partitioning in immiscible silicate-carbonate liquid systems: An initial experimental study using a centrifuge autoclave. *Journal of Petrology*, 1998. 39(11-12): p. 2095-2104.
- Zack, T., S.F. Foley, and G.A. Jenner, A consistent partition coefficient set for clinopyroxene, amphibole and garnet from laser ablation microprobe analysis of garnet pyroxenites from Kakanui, New Zealand. *N. Jb. Miner. Mh.*, 1997. 172: p. 23-41.
- Zack, T., et al., Trace element abundance in rutiles from eclogites and associated garnet mica schists. *Chemical Geology*, 2002. 184: p. 97-122.

10- Melt inclusions:

They provide insight onto igneous processes such as melt generation in the mantle. They are fairly common in minerals such as olivine, plagioclase and zircon. Usually the level of heterogeneities within these melt inclusions exceed the geochemical variety found among bulk rock. Researchers have therefore recently focus their attention on those tiny droplets (usually less than 50 microns) of melts which are supposed to represent instant fraction of the melt generation process. However there are several problems related to the quantification of these melt inclusions using LA-ICP-MS mainly because of their internal chemical

heterogeneity. The most common technique used for the trace element determination of the melt inclusion imply to re-homogenize the inclusions by heating the inclusion after mineral separation, following a careful polishing of the mineral surface down to the inclusion. This technique rely on a complete re-homogenization of melt inclusion during the melting process, followed by the recalculation of the original pre-entrapment of the melt inclusion using their major element composition in Fe.

Otherwise, there are several quantification technique recently reviewed by Halter et al (2002) and which imply the ablation of the inclusion together with the host based on:

- A fixed, pre-determined, concentration of a given element in the melt
- Whole rock differentiation trends in a given igneous suite: if the bulk rocks define a differentiation trend over which one element stay constant, the melt inclusion is assume to their the same chemical characteristic as the bulk rocks and that same constant element could be used for quantification purpose.
- A constant, measured, distribution coefficient between the host and the inclusion melt: this method rely on the knowledge of the concentration of one element in the host (C^{host}) as well as the associated partition coefficient between the host and the melt (D_{elt}). Using the equation below the concentration of that particular element in the melt could be calculated.

$$C_{elt}^{host} = D_{elt} * C_{elt}^{Melt}$$

The determination of the volume ratios between the inclusion and the total ablated volume: This method is fully described in Halter et al (2002) and rely on an accurate determination of that relative volume Mass inclusion/total mass ablated. Using this method, the accuracy will strongly depends on the choice of the internal standard, which should be as different as possible between the melt and the host.

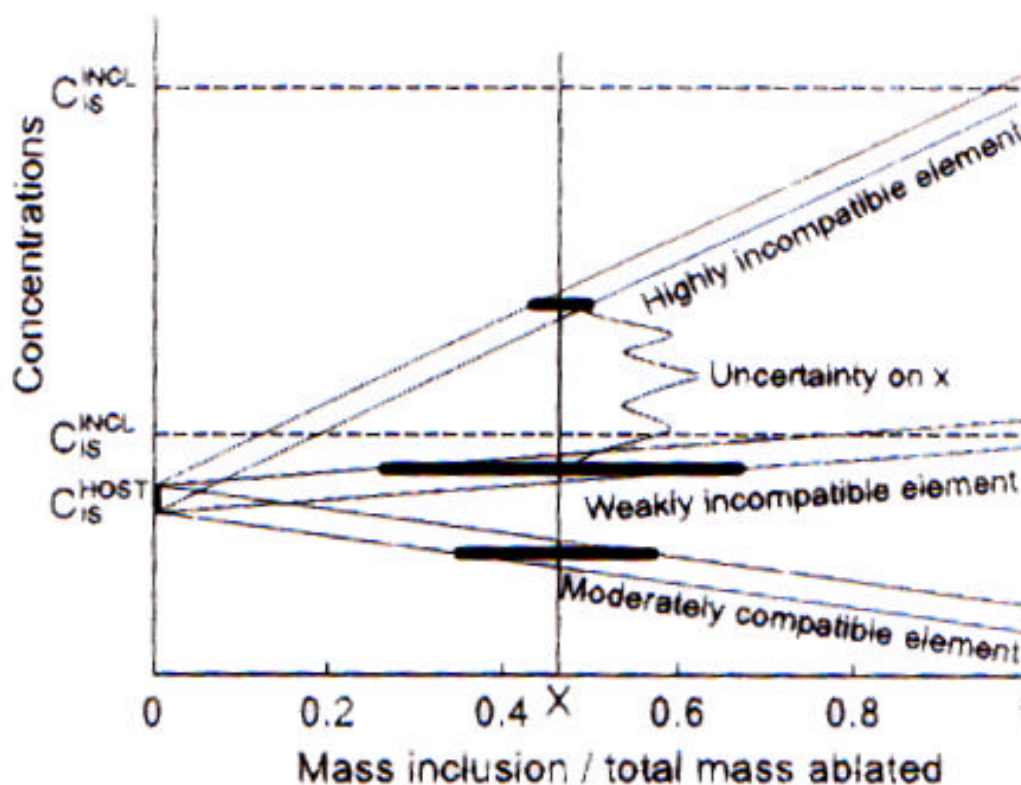


Figure 1-10: Concentration Vs. mass inclusion/total mass ablated. From Halter et al (2002).

Example: melt inclusion in komatiite olivine

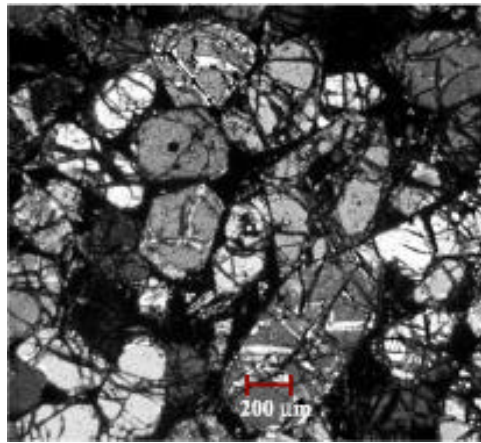


Figure 1-11: Melt inclusion trapped in an olivine within a komatiite.

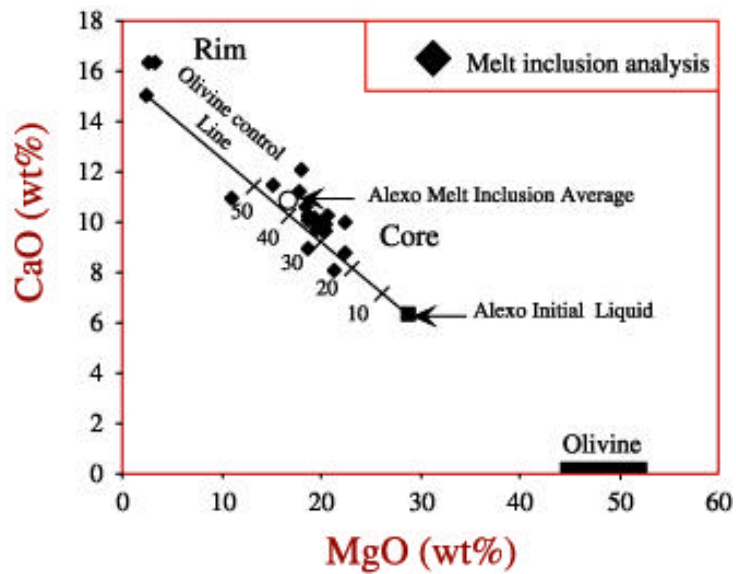


Figure 1-12: CaO Vs. MgO concentration (wt%) in an olivine melt inclusion of a komatiite. The composition of the initial liquid and the host are also shown as well as the degree of olivine fractionation (%).

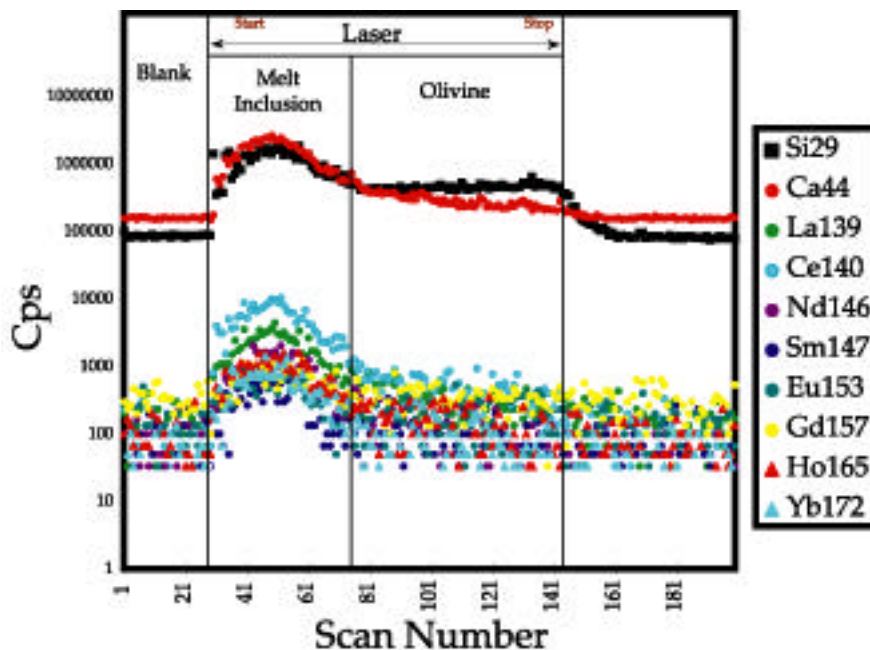


Figure 1-13: Time resolved analysis of a komatiitic melt inclusion.

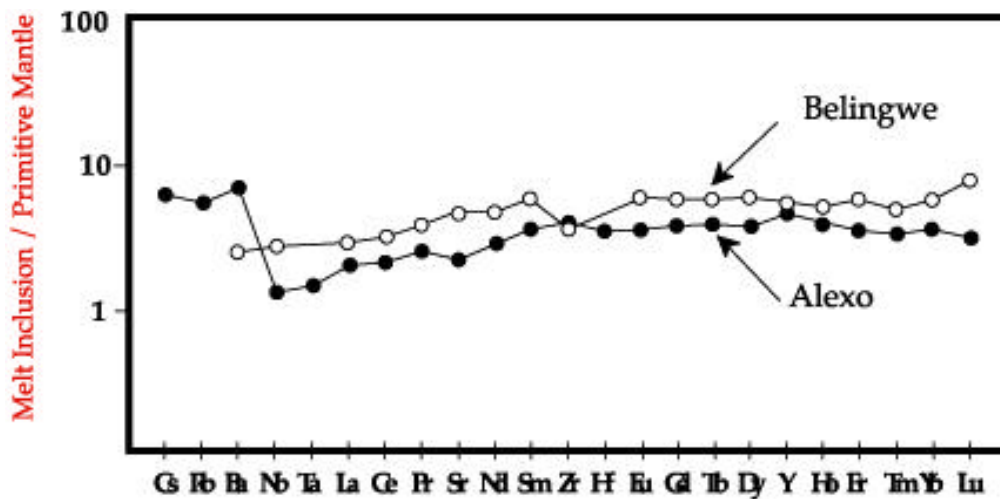


Figure 1-14: Primitive mantle normalised trace element pattern of the Alexo komatiite melt inclusion relative to the Belingwe melt inclusion (McDonough and Ireland, 1993)

- Belfield, S.-J., R.J. Arculus, and S.M. Eggins. Geochemical variation in melt inclusions from the Taupo eruption. in *State of the Arc 2000*. 2000.
- Bryant, C.J., R.J. Arculus, and S.M. Eggins, Laser ablation-inductively coupled plasma-mass spectrometry and tephra: a new approach to understand arc-magma genesis. *geology*, 1999. 27: p. 1119-1122.
- Halter, W.E., et al., Major to trace element analysis of melt inclusions by laser-ablation ICP-MS: methods of quantification. *Chemical Geology*, 2002. 183: p. 63-86.
- Pearce, N.J.G., J.A. Westgate, and W.T. Perkins Developments in the analysis of volcanic glass shards by laser ablation ICP-MS - quantitative and single internal standard multi-elemental methods. *Quaternary International*, 1996. 34: p. 213-227.
- Pereira, C.E.D., et al., Determination of minor and trace elements in obsidian rock samples and archaeological artifacts by laser ablation inductively coupled plasma mass spectrometry using synthetic obsidian standards. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2001. 56: p. 1927-1940.
- Taylor, R.P., et al., In situ trace-element analysis of individual silicate melt inclusions by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS). *Geochimica et Cosmochimica Acta*, 1997. 61(13): p. 2559-2567.

11- Sulphide :

Researchers has mainly focus on the study of the distribution and concentration of PGE in sulphide because of the high partition coefficient for PGE with sulphide. The concentrations should therefore be high enough for a quantification using LA-ICP-MS.

Melting problems

Sulfides have low melting points in comparison with silicate. Melting features such as the one seen on the picture below should be avoided while monitoring power density, laser wavelength, repetition rate etc...

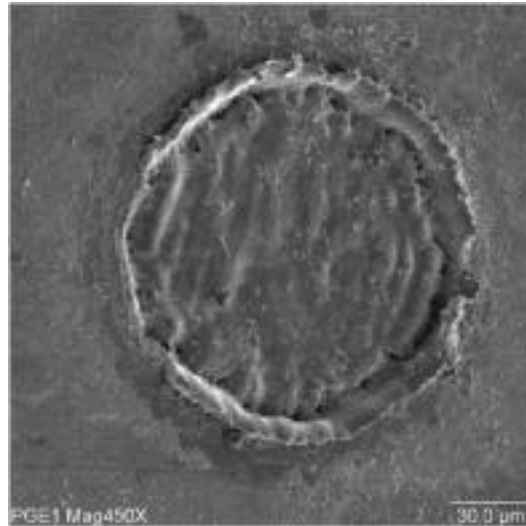


Figure 1-15: 266nm laser ablation pit on a sulphide standard

Interferences problems (Sylvester, GAC MAC volume)

Interferences on Palladium (Cd and ArZn)

$$^{108}\text{Pd}^* = ^{108}\text{Pd}_{\text{meas}} - ^{111}\text{Cd}_{\text{meas}} * (^{108}\text{Cd}/^{111}\text{Cd})$$

$$^{106}\text{Pd}^{**} = ^{106}\text{Pd}^* - [^{40}\text{Ar}^{66}\text{Zn}]_{\text{calc}}$$

$$^{108}\text{Pd}^{**} = ^{108}\text{Pd}^* - [^{40}\text{Ar}^{68}\text{Zn}]_{\text{calc}}$$

$$^{106}\text{Pd}^* = ^{106}\text{Pd}_{\text{meas}} - ^{111}\text{Cd}_{\text{meas}} * (^{106}\text{Cd}/^{111}\text{Cd})$$

Interferences on Rhenium (mono-isotopic element): ArCu on Rh

$$^{103}\text{Rh}^* = ^{103}\text{Rh}_{\text{meas}} - [^{40}\text{Ar}^{63}\text{Cu}]_{\text{calc}}$$

$$[^{40}\text{Ar}^{63}\text{Cu}]_{\text{calc}} = (^{63}\text{Cu}/^{65}\text{Cu}) * [^{40}\text{Ar}^{65}\text{Cu}]_{\text{calc}}$$

$$[^{40}\text{Ar}^{65}\text{Cu}]_{\text{calc}} = ^{105}\text{Pd}_{\text{meas}} - ^{105}\text{Pd}^*$$

$$^{105}\text{Pd}^* = (^{105}\text{Pd}/^{106}\text{Pd}) * ^{106}\text{Pd}^* *$$

Interferences on Ruthenium (Pd and ArNi)

$$^{102}\text{Ru}^* = ^{102}\text{Ru}_{\text{meas}} - ^{102}\text{Pd}^*$$

$$^{102}\text{Pd}^* = (^{102}\text{Pd}/^{106}\text{Pd}) * ^{106}\text{Pd}^* **$$

$$^{101}\text{Ru}^{**} = ^{101}\text{Ru}_{\text{meas}} - [^{40}\text{Ar}^{61}\text{Ni}]_{\text{calc}}$$

$$^{102}\text{Ru}^{**} = ^{102}\text{Ru}^* - [^{40}\text{Ar}^{62}\text{Ni}]_{\text{calc}}$$

$$[^{40}\text{Ar}^{61}\text{Ni}]_{\text{calc}} = (^{63}\text{Ni}/^{65}\text{Ni}) * [^{40}\text{Ar}^{62}\text{Ni}]_{\text{calc}}$$

$$[^{40}\text{Ar}^{62}\text{Ni}]_{\text{calc}} = \frac{(^{101}\text{Ru}/^{102}\text{Ru}) * ^{102}\text{Ru}^* * - ^{101}\text{Ru}}{(^{101}\text{Ru}/^{102}\text{Ru}) - (^{61}\text{Ni}/^{62}\text{Ni})}$$

Standardisation problems

No standard is commercially available. Previous studies have used an inhouse NiS button from the melting of sulfide standards such as SARM7. Balhaus and Sylvester (2000) have produced a PGE-doped Fe-S mixture, annealed in a piston cylinder at 950 °C and 1 GPa for 2 days. Homogeneity is very hard to reach and small scale heterogeneity may remain at the micrometric scale. These heterogeneities may be re-homogenised using a larger spot size during the measurement.

^{34}S or ^{57}Fe could be used as an internal standard since the level of interference is minimal while ablating sulphides.

Example: NiS associated with komatiitic volcanism

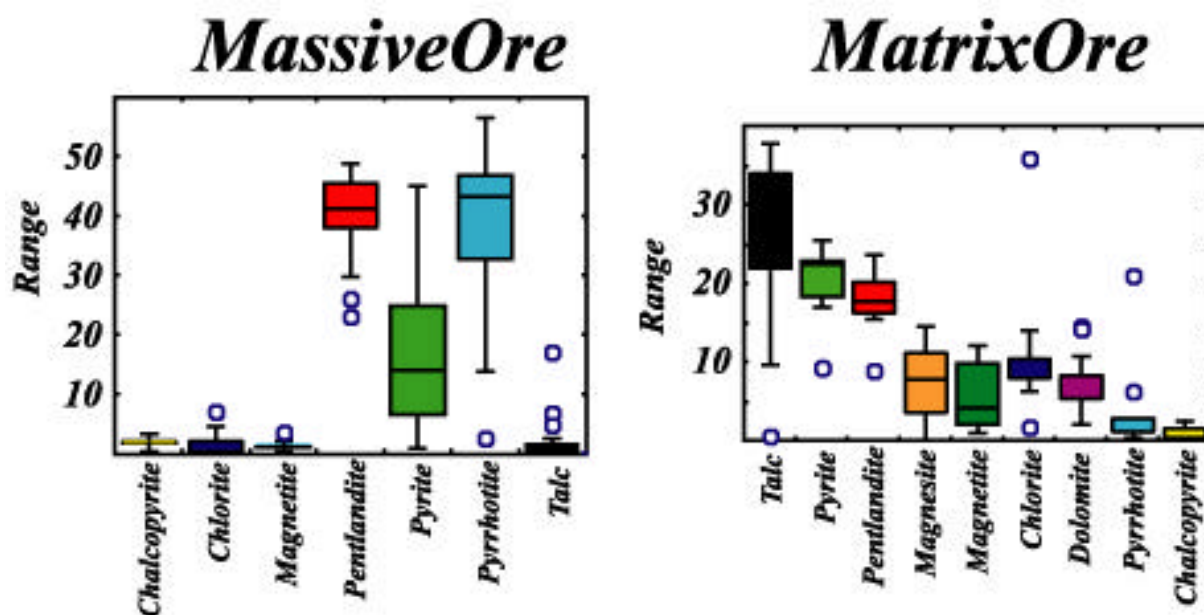


Figure 1-16: Modal abundance of Kambalda NiS.

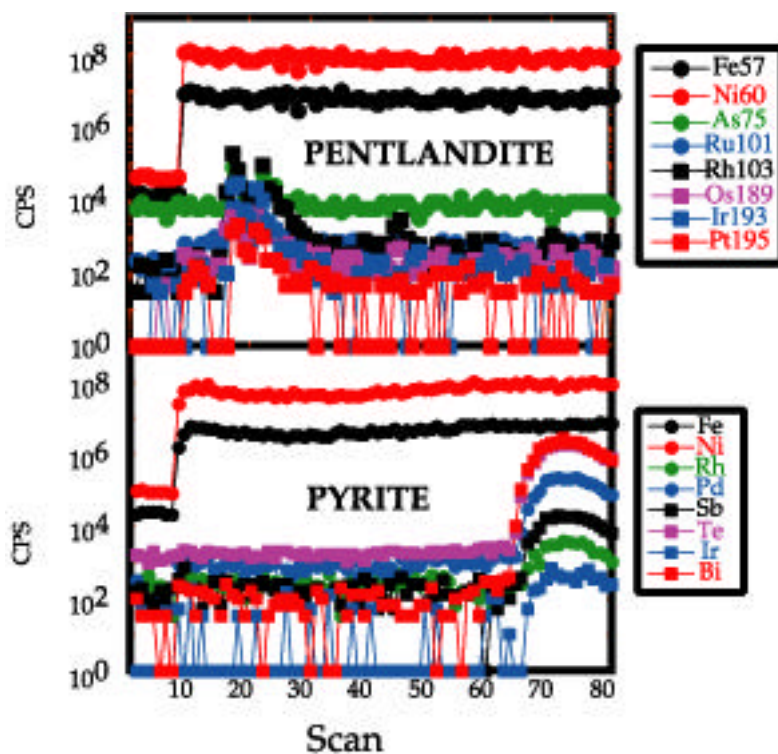


Figure 1-17: PGE distribution within pyrite and pentlandite from the NiS Kambalda area

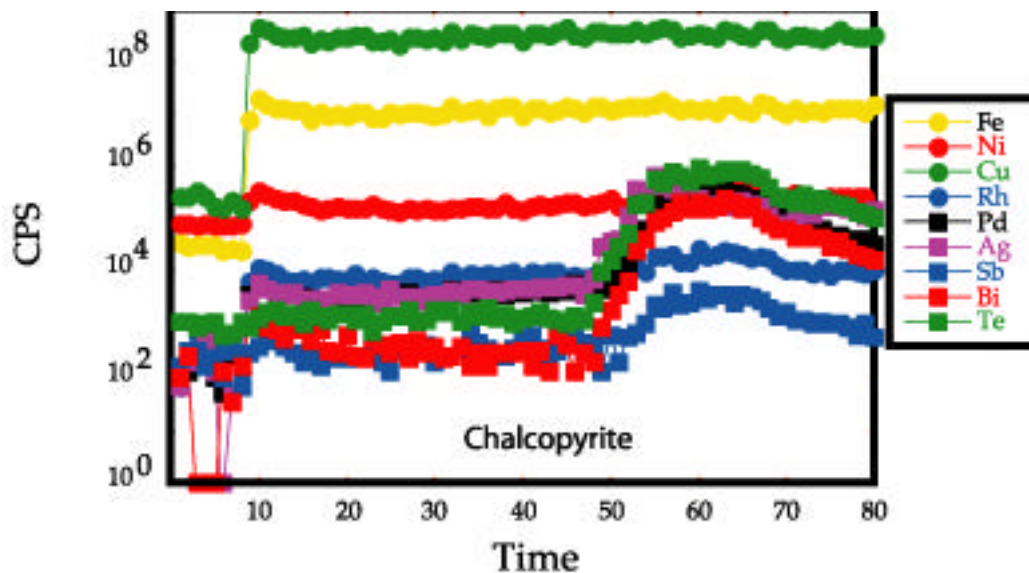


Figure 1-18: PGE distribution within chalcopyrite from the NiS Kambalda area

Variation in PGE and trace element concentration (Count Per Second) within pentlandite, pyrite and chalcopyrite, as determined by LA-HR-ICP-MS.

Laser ablation HR-ICP-MS analysis records PGE concentration through time, as the laser progressively ablates a pit into the sulphide mineral. Data is recorded as counts per second, which is directly proportional to concentration. Perturbations in the concentration of PGE in the time integrated, concentration distribution, are interpreted to represent the presence of micro PGE alloys, or platinum group minerals (PGM). Thus, by this means of analysis we can identify between PGE in PGM, and PGE in solid solution within the host sulphide crystal. The preliminary results of the PGE element distribution within major sulphide phases indicate that most of the P-PGE (Pt, Pd, Rh) are hosted by micro-inclusions of platinum-group minerals, probably secondary in origin. In contrast, the I-PGE (Ir, Os, Ru) are mainly in solid-solution within the major sulphide phases and are inferred to have been immobile.

- Alard, O., et al., Non-chondritic distribution of the highly siderophile elements in mantle sulfides. *Nature*.
- Andras, P., et al., Gold in arsenopyrite from the Pezinok deposit (Western Carpathians, Slovakia) *Geologica Carpathica*, 1995. 46: p. 335-342.
- Axelsson, M.D. and I. Rodushkin, Determination of major and trace elements in sphalerite using laser ablation double focusing sector field ICP-MS. *Journal of Geochemical Exploration*, 2001. 72: p. 81-89.
- Axelsson, M.D., et al., Multi-element analysis of sulphides by ICP techniques and laser ablation. *Recent Res. Devel. Pre & Applied Anal. Chem.*, 2001. 3: p. 27-35.
- Ballhaus, C. and P. Sylvester, Noble metal enrichment processes in the Merensky Reef, Bushveld Complex. *J. Petrology*, 2000. 41: p. 545-561.
- Ballhaus, C., M. Tredoux, and A. Spath, Phase relations in the Fe-Ni-Cu-PGE-S system at magmatic temperature and application to massive sulphide ores of the Sudbury Igneous Complex. *Journal of Petrology*, 2001. 42: p. 1911-1926.
- Butler, I.B. and R.W. Nesbitt, Trace element distributions in the chalcopyrite wall of a black smoker chimney: insights from laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Earth and Planetary Science Letters*, 1999. 167: p. 335-345.
- Chenery, S., et al., Determination of the three-dimensional distributions of precious metals in sulphide minerals by laser ablation microprobe - inductively coupled plasma-mass spectrometry (LAM-ICP-MS). *Chemical Geology*, 1995. 124: p. 55-65.
- de Hoog, J.C.M., P.R.D. Mason, and M.J. van Bergen, Sulfur and chalcophile elements in subduction zones: Constraints from a laser ablation ICP-MS study of melt inclusions from Galunggung Volcano, Indonesia. *Geochimica et Cosmochimica Acta*, 2001. 68: p. 3147-3164.
- Figueiredo, A.M.G., et al., NAA and UV laser ablation ICP-MS for platinum elements and gold determination in NiS fire assay buttons: a comparison between two methods. *Journal of Radioanalytical and Nuclear Chemistry*, 2000. 244(3): p. 623-625.

- Guo, X. and F.E. Lichte, Analysis of rocks, soils and sediments for the chalcophile elements by laser ablation-inductively coupled plasma mass spectrometry. *Analyst*, 1995. 120: p. 2707-2711.
- (Use of Fire assay technique to produce a Nickel sulphide mini bead that will be later on ablated to measure the concentrations of chalcophile elements in various rocks. The heterogeneity within the bead is compensated with a large sample area (10% of the whole bead). The recovery as well is a factor of error and is higher than 95%. The limit of detection for the chalcophile elements are between 1-100 ppb. The main disadvantage of solution analysis is the precipitation of elements such as As and Sb in aqua regia as well as the interferences of Cu and Zn polyatomic species on Ru, Rh and Pd.
- Hall, G.E.M., J.C. Pelchat, and B. Caughlin, Preliminary investigation of a new analytical methodology for the PGEs; laser ablation ICP-MS analysis of partially cupelled lead buttons. *Explore*, 1995. 86: p. 12-17.
- Shibuya, E.K., et al., Determination of platinum group elements and gold in geological materials using an ultraviolet laser ablation high-resolution inductively coupled plasma mass spectrometric technique. *Journal of Analytical Atomic Spectrometry*, 1998. 13(9): p. 941-944.
- Watling, R.C., H.K. Herbert, and I.D. Abell, The application of laser ablation - inductively coupled plasma mass spectrometry (LA-ICP-MS) to the analysis of selected sulphide minerals. *Chemical Geology*, 1995. 124: p. 67-81.
- Watling, R.J., In-line mass transport measurement cell for improving quantification in sulfide mineral analysis using laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 1998. 13(9): p. 927-934.

12- Alloy-metal:

Gold

- Kogan, V.V., M.W. Hinds, and G.I. Ramendik, The direct determination of trace elements in gold and silver materials by laser ablation inductively coupled plasma mass spectrometry without matrix matched. *Spectrochimica Acta*, 1994. 49: p. 333-343.
- McCandless, T.E., M.E. Baker, and J. Ruiz, Trace element analysis of natural gold by laser ablation ICP-MS. *Geostandards Newsletter*, 1997. 21: p. 271-278.
- Outridge, P.M., W. Doherty, and D.C. Gregoire, Determination of trace elemental signatures in placer gold by laser ablation-inductively coupled plasma-mass spectrometry as a potential aid for gold exploration. *Journal of Geochemical Exploration*, 1998. 60(3): p. 229-240.

Alloy

- Becker, J.A., C. Pickhardt, and H.-J. Dietze, Determination of trace elements in high-purity platinum by laser ablation inductively coupled plasma mass spectrometry using solution calibration. *Journal of Analytical Atomic Spectrometry*, 2001. 16: p. 603-606.
- Fairman, B., et al., Industrial analysis: metals, chemicals and advanced materials. *Journal of Analytical Atomic Spectrometry*, 2001. 15: p. 1606-1631.
- Gaegan, M. and J.M. Mermet, Study of laser ablation of brass materials using inductively coupled plasma atomic emission spectrometric detection. *Spectrochimica Acta Part B*, 1998. 53: p. 581-591.
- Raith, A., et al., Non-destructive sampling method of metals and alloys for laser ablation-inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 1995. 10: p. 591-594.

13- Depth profiling:

- Bi, M., et al., Profiling of patterned metal layers by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Applied Surface Science*, 2000. 158: p. 197-204.
- Bleiner, D., et al., Depth profile analysis of various titanium based coatings on steel and tungsten carbide using laser ablation inductively coupled plasma - "time of flight" mass spectrometry. *Fresenius Journal of Analytical Chemistry*, 2000. 368: p. 221-226.

- Kanicky, V., V. Otruba, and J. Mermet, Analysis of tungsten carbide coatings by UV laser ablation inductively coupled plasma atomic emission spectrometry. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2000. 55(6): p. 575-586.
- Liu, H.C., et al., Early phase laser induced plasma diagnostics and mass removal during single-pulse laser ablation of silicon. *Spectrochimica Acta Part B*, 1999. 54: p. 1607-1624.
- Mank, A.J.G. and P.R.D. Mason, A critical assessment of laser ablation ICP-MS as an analytical tool for depth analysis in silica-based glass samples. *Journal of Analytical Atomic Spectrometry*, 1999. 14(8): p. 1143-1153.
- Eggins, S.M., L.P.J. Kinsley, and J.M.G. Shelley, Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS. *Applied Surface Science*, 1998. 129: p. 278-286.

14- Forensic science

- Watling, R.J., B.F. Lynch, and D. Herring, Use of laser ablation inductively coupled plasma mass spectrometry for fingerprinting scene of crime evidence. *Journal of Analytical Atomic Spectrometry*, 1997. 12: p. 195-203.
- Watling, R.J., Sourcing the provenance of cannabis crops using inter-element association patterns "fingerprinting" and laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 1998. 13(9): p. 917-926.

15- Gemology

Comparison between synthetic and natural sapphire and ruby.

The natural gems (Rwanda, Burma sapphire and Mong Hsu ruby) tends to show a higher concentration in Fe and Ga. The synthetic gems (Novosibirsk ruby, Star Brown and Verneuil pink sapphire) are poor in Fe, Ga but show elevated concentrations in V, Nb and W. The enrichments in those elements not likely reflect the conditions of the synthesis (autoclave compositions). However due to the lack of proper standard for this study, the value presented here shouldn't be consider as true concentration on elements with low abundance and which suffer from large interferences. The use of higher resolution is required in order to produce calibration line with low intercept.

16- Weathering processes:

Example from the opal chemistry in Australia.