

Day 5

Applications for LA-(MC)-ICP-MS

(text need some serious improvement)

Stable isotopes:

Li

The two isotopes of lithium (7.5% of ^6Li and 92.5% of ^7Li) have a relative mass difference of approximately 16.6% (larger than B with 10% and ^{16}O - ^{18}O with 12.5%). Hence Li isotopic fractionation seems to be a promising tool to monitor low surface chemical processes. Lithium isotopic composition varies within 60 ‰ in nature. At higher temperature, the fractionation factor approach unity and crystal-liquid fractionation are smaller than 1 ‰. With the development of MCICPMS, the related increase in the precision of the $^6\text{Li}/^7\text{Li}$ ratio measurement (0.5 ‰, 2 σ) and since olivine is the major Li host in the mantle, recent research focus on the upper mantle fractionation of the Li isotopes as a tracer of magmatic processes in peridotite and specially in arc environments. No laser ablation studies have been conducted so far on the lithium isotopic composition of mantellic material using laser ablation mainly because of the low Li concentration of the olivine (few ppm) and the lack of internal mass bias correction.

Reference:

- Bouman, C., P. Z. Vroon, et al. (2002). Determination of lithium isotope compositions by MC-ICP-MS (Thermo Finnigan MAT Neptune). Goldschmidt conference abstract, Davos.
- Marriott, C. S., N. S. Belshaw, et al. (2002). Lithium and calcium isotope fractionation in inorganically precipitated calcite: assessing their potential as a paleothermometer. Goldschmidt conference abstract, Davos.
- Tomascak, P. B., J. G. Ryan, et al. (2000). "Lithium isotope evidence for light element decoupling in the Panama subarc mantle." *Geology* 28: 507-510.
- Nishio, Y. and S. Nakai (2002). "Accurate and precise lithium isotopic determinations of igneous rock samples using multi-collector inductively coupled plasma mass spectrometry." *Analytica Chimica Acta* 456: 271-281.
- Tomascak, P. B., R. W. Carlson, et al. (1999). "Accurate and precise determination of Li isotopic compositions by multi-collector sector ICP-MS." *Chemical Geology* 158: 145-154.
- Tomascak, P. B., J. G. Ryan, et al. (2000). "Lithium isotope evidence for light element decoupling in the Panama subarc mantle." *Geology* 28: 507-510.
- Tomascak, P. B., F. Tera, et al. (1999). "The absence of lithium isotope fractionation during basalt differentiation: New measurements by multicollector sector ICP-MS." *Geochimica et Cosmochimica Acta* 63: 907-910.
- Tomascak, P. B., E. Widom, et al. (2002). "The control of lithium budgets in island arcs." *Earth & Planetary Science Letters* 196: 227-238.

B

The two isotopes of Boron (19.9% of ^{10}B and 80.1% of ^{11}B) have a relative mass difference of approximately 10%. A very large isotopic fractionation of the B isotopes is observed in the nature, from +60‰ in marine evaporitic brines to -30‰ in non-marine evaporites mainly because of its mobility during both magmatic and fluid related processes within a large temperature range. The B isotopic fractionation is relatively insensitive to oxydo-reduction reactions. Ion probe techniques provide poor precision (3‰ at 2s) and time consuming TIMS analyses involve positive ions from alkali borates provide reproductibilities for the standard 951 from 0.2‰ to 1‰ (2s). More recent TIMS techniques using negative ions provide better precision (<0.7‰). Lécuyer et al (2002) have recently developed a simple protocol for the chemical separation of B from seawater, carbonate, phosphate and silicates, which provide an external reproductibility on the standard 951 of ± 0.3 ‰ at 2 σ using a MCICPMS. This method requires at least 2 μg of B from the starting material. No laser ablation boron isotope analyses has been conducted so far although this technique has great potential for the isotopic measurement of B-rich phases such as tourmalines, which are also hard to dissolve using basic wet chemistry procedures. Tourmaline is an ideal petrogenetic and ore-genetic tracer and its isotopical composition may record the primary isotopical signature of the hydrothermal ore-forming event, due to its refractory nature that is hardly altered

though post-ore hydrothermal alteration and metamorphism (Jiang 2001, *Phys. Chem. Earth*, 26:851-858).

Reference:

- Aggarwal, J. K., K. Mezger, et al. (1999). "Precise and accurate determination of boron isotope ratios by multiple collector ICP-MS: origin of boron in the Ngawha geothermal system, New Zealand." *ES transaction*.
- Lécuyer, C., P. Grandjean, et al. (2002). "¹¹B/¹⁰B analysis of geological materials by ICP-MS plasma 54: application to the boron fractionation between brachiopod calcite and seawater." *Chemical Geology* 186: 45-55.

Mg

Magnesium has 3 naturally occurring isotopes ²⁴Mg, ²⁵Mg and ²⁶Mg, with relative abundance of 78.99%, 10% and 11.01%, respectively. Natural variations of the isotopic composition of Mg may arise through (Galy et al, 2001):

- Stellar nucleosynthesis and incorporation of pre-solar grains into meteorites
- The decay of ²⁶Al to ²⁶Mg
- Isotopic fractionation through volatilization / condensation reactions
- Isotope fractionation during low temperature fluid/rock interactions
- Kinetic and thermodynamic isotope effects accompanying biological incorporation and rejection

Previous analyses using TIMS have shown relatively low terrestrial variations (few ‰) with a error of (1‰ to 2‰). Recent MCICPMS studies have demonstrated a repeatability of the standard SRM 980 between 0.12‰ and 0.06‰ (Galy et al, 2001). Galy et al have shown a terrestrial variability on ²⁶Mg of 4‰ for nine samples. More recently Galy et al (2002) have demonstrated a 4.13‰ and 2.14‰ isotopic variations respectively for d²⁶Mg and d²⁵Mg while analysing speleothems and their associated host-rocks and waters.

$$\delta^x \text{Mg} = \left(\frac{({}^x \text{Mg} / {}^{24} \text{Mg})_{\text{sample}}}{({}^x \text{Mg} / {}^{24} \text{Mg})_{\text{SRM 980}}} - 1 \right) * 1000$$

$$X = 25 \text{ or } 26$$

The main analytical problems with Mg isotopes measurements are related to the presence of molecular interferences on all isotopes, instrumental fractionation and matrix effects. Galy et al (2001) have shown that matrix effects are relatively significant and that only magnesia, magnesite and chlorophyll would permit a direct measurement without previous chemical separation of Mg. The use of high resolution instrument to correct for the interferences might improve this matrix dependency. Young et al (2002) have analyzed Mg isotopic composition of the Allende meteorite using laser ablation MCICPMS and represent so far the only published result on in-situ measurement. For this particular experiment, the addition of concomitant element during the ablation didn't significantly shift the Mg isotopic composition.

Reference:

- Alard, O., K. W. Burton, et al. (2002). Mg-isotopes in terrestrial and extraterrestrial olivine. Goldschmidt conference abstract, Davos.
- Chang, V. T.-C., N. Belshaw, et al. (2002). Mg and Ca isotope fractionation during CaCO₃ biomineralization. Goldschmidt conference abstract, Davos.
- Galy, A., N. S. Belshaw, et al. (2001). "High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry." *Int. J. Mass Spectrom* 208: 89-98.
- Galy, A. (2002). Isotopic composition of dissolved Mg in natural waters. Goldschmidt conference abstract, Davos.
- Galy, A., M. Bar-Matthews, et al. (2002). "Mg isotopic composition of carbonate: insight from speleothem formation." *EPSL* 201: 105-115.

Young, E. D., R. D. Ash, et al. (2002). "Mg isotope heterogeneity in Allende meteorite measured by UV laser ablation-MC-ICPMS and comparisons with O isotopes." *Geochimica et Cosmochimica Acta* 66: 683-698.

Si

Silica is the second most abundant element after oxygen in the silica Earth and its isotopic composition is of major interest for a large range of topics in the Earth sciences, ranging from continental weathering to biological productivity in the ocean (Vroon et al, 2002). The three isotopes of silica (92.23% of ^{28}Si , 4.67% of ^{29}Si and 3.1% of ^{30}Si) have a relative mass difference of approximately 7% between ^{28}Si and ^{30}Si . Not much information is available from the literature about the natural isotopic variation of Si isotopes. Ziegler et al (2002) have noticed up to -1.5‰ Si-isotopic differences between solutions and solids in weathered soil profiles. These measurements suffer from classic polyatomic interferences such as CO, N₂ on ^{28}Si and ^{29}Si ; CO, NO and N₂H on ^{30}Si . Using High resolution (Vroon et al, 2000) obtain a reproductibility better than 0.17‰ on a 10ppm solution for a 3 hour measurement. Using a Nu and its zoom optics, Alleman et al (2002) were able to measure Si isotopes in dynamic mode, while monitoring the Mg isotopes as an internal standard. In this last experiment, the reproductibility were better than 0.15‰ and individual precision better than 0.05‰. the mass bias for this mass range is about 12%.

Reference:

- Alleman, L., D. Cardinal, et al. (2002). New developments in measuring silicon isotopes by MC-ICP-MS. Goldschmidt conference abstract, Davos.
- Vroon, P. Z., C. J. Beets, et al. (2002). Silicon isotopic composition of sponge spicules determined by MC-ICPMS. Goldschmidt conference abstract, Davos.
- Ziegler, K., O. A. Chadwick, et al. (2002). The ^{30}Si values of soil weathering profiles: indicators of Si pathways at the lithosphere/hydro(bio)sphere interface. Goldschmidt conference abstract, Davos.

Ca

Calcium is the fifth most abundant element in the silicate Earth (after O, Si, Al, Fe). Calcium has six stable isotopes (96.941% of ^{40}Ca , 0.647% of ^{42}Ca , 0.135% of ^{43}Ca , 2.086% of ^{44}Ca , 0.004% of ^{46}Ca , 0.187% of ^{48}Ca) and a relative mass difference of 4.7% between ^{42}Ca and ^{44}Ca . A study of Ca isotopes in natural samples reveals a variation up to 4‰ on $^{44}\text{Ca}/^{40}\text{Ca}$ using TIMS. Due to isobaric interference of ^{40}Ca and ^{40}Ar the natural variation measured by ICP between $^{44}\text{Ca}/^{42}\text{Ca}$ is assumed to be smaller. Using double Ca spike for mass fractionation correction, TIMS measurements reach the precision of 0.1‰ although more recent TIMS analyses claim precision down to 25 ppm (Tuttas & Shwieters, Goldsmidt 2002). Ca isotope fractionation has been observed in environmental samples as well as in medical applications.

Reference:

- Halicz, L., A. Galy, et al. (1999). "High-precision measurement of calcium isotopes in carbonates and related material by multi collector inductively coupled plasma mass spectrometry." *Journal of Analytical Atomic Spectrometry* 14: 1835-1838.
- Marriott, C. S., N. S. Belshaw, et al. (2002). Lithium and calcium isotope fractionation in inorganically precipitated calcite: assessing their potential as a paleothermometer. Goldschmidt conference abstract, Davos.

Ti

The five isotopes of titanium (8% of ^{46}Ti , 7.3% of ^{47}Ti , 73.8% of ^{48}Ti , 5.5% of ^{49}Ti and 5.4% of ^{50}Ti) have a relative mass difference of approximately 8.7% between ^{46}Ti and ^{50}Ti . The Ti isotopic system is largely unexplored although titanium is an element of considerable geochemical and cosmochemical importance (Guo et al, 2002). Development in solution MCICPMS unable long term reproductibility of ^{47}Ti , ^{48}Ti , ^{49}Ti and ^{50}Ti respectively at 0.4, 0.6, 0.7 and 0.8 unit:

$$\epsilon^{x}\text{Ti} = \left(\left(\frac{{}^x\text{Ti}/{}^{46}\text{Ti}}{\text{sample}} \right) / \left(\frac{{}^x\text{Ti}/{}^{46}\text{Ti}}{\text{standard}} \right) - 1 \right) * 10000$$

An overall variation of about 50Ti units has been observed between a variety of samples such as basalts, mantle xenoliths, loess, chondrites and achondrites (Guo et al, 2002).

Reference:

Chen, H.-W. and T. Lee (2002). Pitfalls of Ti isotopic measurement by multi-collector-ICP-MS. Goldschmidt conference abstract, Davos.

Guo, Y., A. Makishima, et al. (2002). High precision measurement of Ti isotopes in terrestrial and extraterrestrial materials. Goldschmidt conference abstract, Davos.

Fe

Iron is the fourth most abundant element in the silicate Earth and have four stable isotopes (5.8% of ^{54}Fe , 91.72% of ^{56}Fe , 2.2% of ^{57}Fe , 0.28% of ^{58}Fe) and a relative mass difference of 7.4% between ^{54}Fe and ^{58}Fe .

Reference:

Matthews, A., H. Morgans-Bell, et al. (2002). Cyclic variations of iron isotope composition during diagenesis: the Kimmeridge clay formation (UK). Goldschmidt conference abstract, Davos.

Mullane, E., R. J. Herrington, et al. (2002). Iron isotope fractionation in an Archaean BIF sample suite. Goldschmidt conference abstract, Davos.

Ohno, T., I. Kouge, et al. (2002). Iron isotopes in human blood. Goldschmidt conference abstract, Davos.

Poitrasson, F., N. Teutsch, et al. (2002). Iron isotope signature of the inner solar system. Goldschmidt conference abstract, Davos.

Von Blanckenburg, F. and T. Walczyk (2002). Iron isotope fractionation by the human body, animals and plants. Goldschmidt conference abstract, Davos.

Wiederhold, J. G. and F. Von Blanckenburg (2002). Iron isotope variations in a complete natural soil catena with lateral iron mobilization and reprecipitation. Goldschmidt conference abstract, Davos.

Williams, H., D.-C. Lee, et al. (2002). Iron isotope composition of mid-ocean ridge basalts and mantle peridotites. Goldschmidt conference abstract, Davos.

Zhu, X. K., R. K. O'Nions, et al. (2000). "Secular variation of iron isotopes in North Atlantic Deep Water." *Science* 287: 2000-2002.

Ni

Quitté, G. and A. N. Halliday (2002). Nickel isotopes in meteorites: constraints on the early solar system. Goldschmidt conference abstract, Davos.

Cu & Zn

Copper has two stable isotopes of mass 63 and 65, whose average abundances are 69.17% and 30.83% respectively (Shields et al, 1964). Zinc has five isotopes of mass 64, 66, 67, 68 and 70, whose average abundances are 48.63%, 27.90%, 4.10%, 18.75% and 0.62% respectively. Natural isotopic variation between silicate, ores, sediments, biological materials are within a few ‰. These 2 isotopic system are potentially useful geochemical and biological tracers.

Reference:

Gale, N. H., A. P. Woodhead, et al. (1999). "Natural variations detected in the isotopic composition of copper . possible applications to archaeology and geochemistry." *International Journal of Mass Spectrometry* 184: 1-9.

Maréchal, C. and F. Albarède (2002). "Ion-exchange fractionation of copper and zinc isotopes." *Geochimica et Cosmochimica Acta* 66: 1499-1509.

Maréchal, C. N., E. Nicolas, et al. (2000). "Abundance of zinc isotopes as a marine biochemical tracer." *G3* 1.

Zhu, X. K., R. K. O'Nions, et al. (2000). "Determination of natural Cu-isotope variation by plasma-source mass spectrometry : implications for use as geochemical tracers." *Chemical Geology* 163: 139-149.

Zhu, X. K., R. J. P. Williams, et al. (2002). "Mass fractionation processes of transition metal isotopes." *EPSL* 200: 47-62.

Ge

Reference:

Galy, A., O. S. Pokrovsky, et al. (2002). Ge-isotopic fractionation during its sorption on goethite: an experimental study. Goldschmidt conference abstract, Davos.

Hirata, T. (1997). "Isotopic variations of germanium in iron and stony iron meteorites." *Geochimica et Cosmochimica Acta* 61: 4439-4448.

Se

The six isotopes of selenium (0.89% of ^{74}Se , 9.36% of ^{76}Se , 7.63% of ^{77}Se , 23.78% of ^{78}Se , 49.61% of ^{80}Se and 8.73% of ^{82}Se) have a relative mass difference of approximately 11% between ^{74}Se and ^{80}Se . Due to the low isotopical abundance of ^{74}Se , ^{76}Se is preferred (about 8% relative mass difference). Because of its toxicity, its different valence state and its large number of isotopes, selenium is a potential tracer of geological and biological tracer (Rouxel et al, 2002). Using a new pre-concentration and separation technique Rouxel et al (2002) were able to measure the different selenium isotopes with an external precision of 0.25‰. The overall isotopical variation from environmental, deep-sea sediments, hydrothermal deposits, igneous rocks and meteorites are about 8‰ on $^{82}/^{76}\text{Se}$. No experiments have been conducted so far with laser ablation.

Reference:

Rouxel, O., J. Ludden, et al. (2002). "Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry." *GCA* 66: 3191-3199.

Cd

Reference:

Cloquet, C., J. Carignan, et al. (2002). High precision cadmium isotopic measurements by MC-ICP-MS. Goldschmidt conference abstract, Davos.

Wombacher, F., M. Rehkamper, et al. (2002). Stable isotope compositions of cadmium in stony meteorites. Goldschmidt conference abstract, Davos.

Sn

Reference:

Lee, D.-C. and A. N. Halliday (1995). "Precise determinations of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass spectrometry." *International Journal of Mass spectrometry and ion Processes* 146/147: 35-46.

Nd

Reference:

Luais, B., P. Telouk, et al. (1997). "Precise and accurate neodymium isotopic measurements by plasma-source mass spectrometry." *Geochimica Cosmochimica Acta* 61: 4847-4854.

Vance, D. and M. Thirlwall (2002). "An assessment of mass discrimination in MC-ICPMS using Nd isotopes." *Chemical Geology* 185: 227-240.

Ag

Reference:

Woodland, S. J., M. Rehkamper, et al. (2002). High precision MC-ICP-MS measurement of Ag isotopic ratios. Goldschmidt conference abstract, Davos.

Hg

Reference:

Evans, R. D. and P. J. Dillon (2002). Determination of variations in isotope ratios of Hg. Goldschmidt conference abstract, Davos.

Tl

Reference:

Nielsen, S. G., M. Rehkämper, et al. (2002). Isotopic compositions and concentrations of estuarine thallium. Goldschmidt conference abstract, Davos.

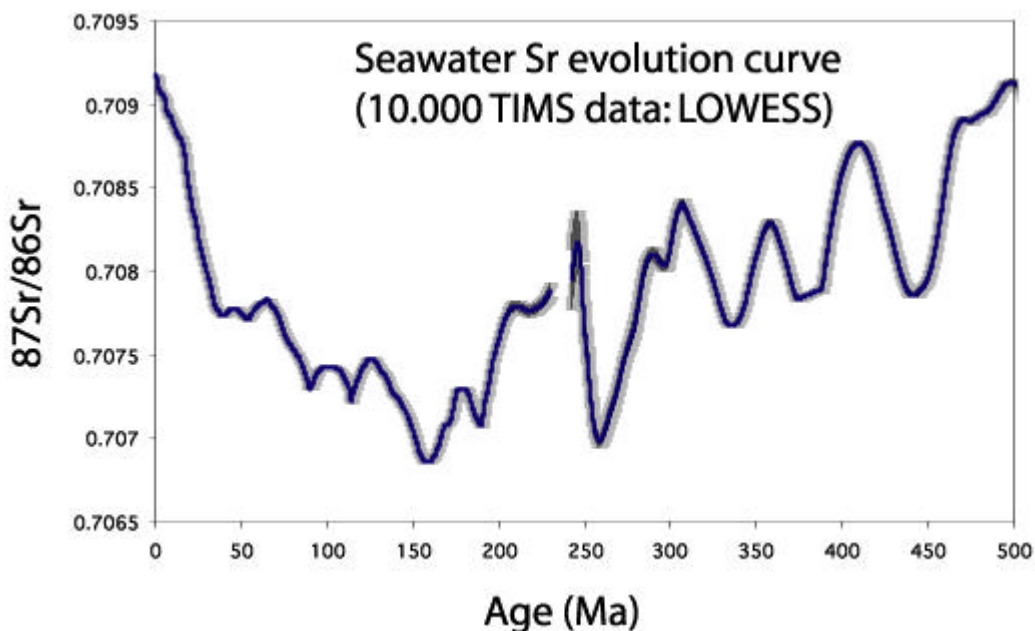
Rehkämper, M. and A. N. Halliday (1999). "The precise measurement of Tl isotopic compositions by MC-ICPMS: Application to the analysis of geological materials and meteorites." *Geochimica et Cosmochimica Acta* 63: 935-944.

Radiogenic isotopes: **Sr**

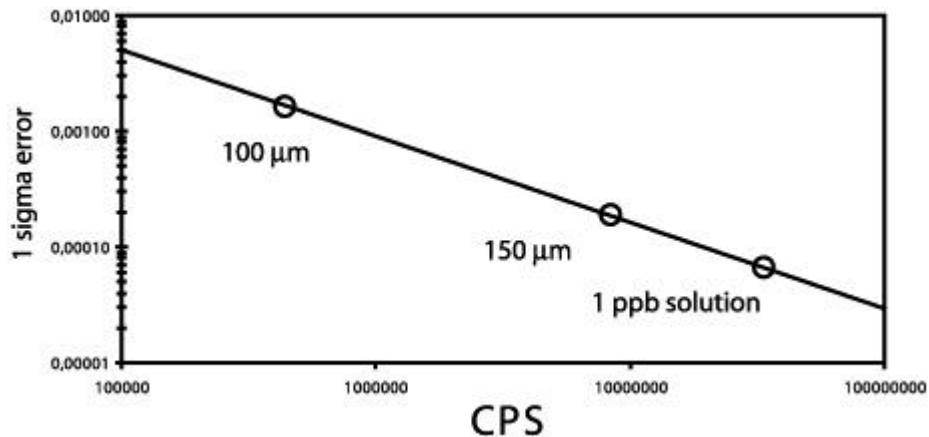
Strontium isotopic composition is an important geochemical tracer. It is used in a wide range of applications, including tracing water sources, mantle processes and in geochronological systems of Rb-Sr. The natural variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is derived from the radioactive decay of ^{87}Rb to ^{87}Sr (Ehrlich et al, 2001). Strontium has 4 isotopes (0.56% of ^{84}Sr , 9.86% of ^{86}Sr , 7% of ^{87}Sr and 82.58% of ^{88}Sr), 3 of which are stable (^{84}Sr , ^{86}Sr and ^{88}Sr). TIMS is commonly used for precise Sr isotopic measurements with internal and external precision respectively of about 0.02‰ and 0.01‰. Ehrlich et al (2001) have recently discussed on the isotopic measurement using MCICPMS and claim a precision of about 0.02‰ using a faster acquisition time and higher TDS samples. The precision of Sr isotopes is facilitated by the use of an internal stable isotopic pair ($^{84}\text{Sr}/^{88}\text{Sr}$) to correct for the mass bias of the instrument. Recently the Rb-Sr isotopic measurement has been improved by using a Zr spike while measuring Rb isotopic composition (Waight et al, 2002). Also be careful about the Kr correction on ^{86}Sr (see earlier section on interferences). The Sr isotopes composition could be used either as an isotopic tracer while ablating calcium, phosphate-rich material (plagioclase, apatite, bones etc..) or as a geochronometer together with Rb isotopes. The following are just some examples of applications.

- Sr isotopes fingerprinting of magmatic processes through the in-situ analysis of Sr isotopic composition of plagioclase.
- Sr isotopes geochronology on Palaeozoic carbonates ?

In marine carbonate, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio reflects the isotopic composition of sea-water from which they precipitate. Over geological history, the isotopic composition of sea-water has varied considerably (see figure below) and thus, the isotopic composition of Sr in carbonates is a useful tool in reconstruction of geological history. Strontium isotope stratigraphy is finding widespread use for dating and correlation of sediments.



Sea-water Sr evolution curve for the Palaeozoic (McArthur publications)



Error on $^{87}/^{86}\text{Sr}$ determination at variable spot size and with 1ppb solution for 3 mn acquisition.

-Sr isotopic in skeletal elements (bones, teeth etc..) could be useful to infer the geographic region that an animal or human inhabited, because different regions tend to have distinct Sr isotopic compositions.

Reference:

- Christensen, J. N., A. N. Halliday, et al. (1995). "In situ Sr isotopic analysis by laser ablation." *Earth and Planetary Science Letters* 136(1-2): 79-85.
- Davidson, J. P., F. J. Tepley III, et al. (2001). "Magma recharge, contamination and residence times revealed by in-situ laser ablation isotopic analysis of feldspar in volcanic rocks." *Earth and Planetary Science Letters* 184(427-442).
- Prohaska, T., C. Latkoczy, et al. (2002). "Investigation of Sr isotope ratios in prehistoric human bones and teeth using laser ablation ICP-MS and ICP-MS after Rb/Sr separation." *JAAS* 17(8): 887-891.
- Ehrlich, S., I. Gavioli, et al. (2001). "Direct high-precision measurements of the Sr-87/Sr-86 isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS)." *Journal of Analytical Atomic Spectrometry* 16: 1389-1392.
- Waight, T., J. A. Baker, et al. (2002). "Rb isotope dilution analyses by MC-ICP-MS using Zr to correct for mass fractionation: towards improved Rb-Sr geochronology ?" *Chemical Geology* 186: 99-116.

Zr

Reference:

- Hirata, T. and T. Yamaguchi (1999). "Isotopic analysis of zirconium using enhanced sensitivity-laser ablation-multiple collector-inductively coupled plasma mass spectrometry." *Journal of Analytical Atomic Spectrometry* 14: 1455-1459.
- Hirata, T. (2001). "Determinations of Zr isotopic compositions and U-Pb ages for terrestrial and extraterrestrial Zr-bearing minerals using laser ablation-inductively coupled plasma mass spectrometry: implications for Nb-Zr isotopic systematics." *Chemical Geology* 176: 323-342.
- Sanloup, C., J. Blichert-Toft, et al. (2000). "Zr anomalies in chondrites and the presence of ^{92}Nb in the early solar system." *Earth and Planetary Science Letters*: 75-81.

Mo

Reference:

- Barling, J., G. L. Arnold, et al. (2001). "Natural mass-dependent variations in the isotopic composition of molybdenum." *EPSL* 193: 447-457.
- Lee, D.-C. and A. N. Halliday (1995). "Precise determinations of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector

multiple collector mass spectrometry." *International Journal of Mass spectrometry and ion Processes* 146/147: 35-46.

Siebert, C., T. F. Nägler, et al. (2001). "Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry." *G3* 2.

Siebert, C., T. F. Nägler, et al. (2002). The oceanic Mo cycle over the last 60a. Goldschmidt conference abstract, Davos.

Pd

Reference:

Carlson, R. W. and E. H. Hauri (2001). "Extending the Pd-107-Ag-107 chronometer to low Pd/Ag meteorites with multicollector plasma-ionization mass spectrometry." *Geochimica Cosmochimica Acta* 65(11): 1839-1848.

Hf

Reference:

Albarède, F., J. Blichert-Toft, et al. (2000). "Hf-Nd isotope evidence for a transient dynamic regime in the early terrestrial mantle." *Nature* 404: 488-490.

Griffin, W. L., N. J. Pearson, et al. (2000). "The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites." *Geochimica et Cosmochimica Acta* 64: 133-147.

Blichert-Toft, J., F. A. Frey, et al. (1999). "Hf isotope evidence for pelagic sediments in the source of Hawaiian." *Science* 285: 879-882.

Blichert-Toft, J. and F. Albarède (1997). "The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system." *Earth and Planetary Science Letters* 148: 243-258.

Blichert-Toft, J., F. Albarède, et al. (1999). "The Nd and Hf isotopic evolution of the mantle through the Archean. Results from the Isua supracrustals, West Greenland, and from the Birimian terranes of West Africa." *Geochimica et Cosmochimica Acta* 63: 3901-3914.

Blichert-Toft, J. and N. T. Arndt (1999). "Hf isotope compositions of komatiites." *Earth & Planetary Science Letters* 171(3): 439-451.

Blichert-Toft, J., C. Chauvel, et al. (1997). "Separation of Hf and Lu for high-precision analysis of rock samples by magnetic sector-multiple collector ICP MS." *Contribution to Mineralogy and Petrology* 127: 248-260.

Lee, D.-C., A. N. Halliday, et al. (1999). "Hafnium isotope stratigraphy of ferromanganese crusts." *Science* 285: 1052-1054.

Lee, D.-C. and A. N. Halliday (1996). "Hf-W isotopic evidence for rapid accretion and differentiation in the Early Solar System." *Science* 274: 1876-1879.

Lee, D.-C. and A. N. Halliday (2000). "Hf-W internal isochrons for ordinary chondrites and the initial $^{182}\text{Hf}/^{180}\text{Hf}$ of the solar system." *Chemical Geology* 169: 35-43.

Stevenson, R. K., M. Bizzaro, et al. (2002). Hf isotope composition of 3Ga komatiites from Ontario, Canada. Goldschmidt conference abstract, Davos.

Thirlwall, M. F. and A. J. Walder (1995). "In situ hafnium isotope ratio analysis of zircon by inductively coupled plasma multiple collector mass spectrometry." *Chemical Geology* 122(1-4): 241-247.

Vervoort, J. D., P. J. Patchett, et al. (2000). "Hf-Nd isotopic evolution of the lower crust." *Earth and Planetary Science Letters* 181: 115-129.

W

Reference:

Halliday, A. N. (2000). "Hf-W chronometry and inner solar system accretion rates." *Space Science Reviews* 92: 355-370.

Halliday, A. N. and D. C. Lee (1999). "Tungsten isotopes and the early development of the Earth and Moon." *Geochimica et Cosmochimica Acta* 63: 4157-4179.

Quitté, G., J.-L. Birk, et al. (2000). " ^{182}Hf - ^{182}W systematics in eucrites: the puzzle of iron segregation in the early solar system." *Earth and Planetary Science Letters* 184: 83-94.

Os

Reference:

Alard, O., W. L. Griffin, et al. (2000). "Non-chondritic distribution of the highly siderophile elements in mantle sulfides." *Nature* 407: 891-894.

- Hirata, T., M. Hattori, et al. (1998). "In-situ osmium isotope ratio analyses of iridosmines by laser ablation-multiple collector-inductively coupled plasma mass spectrometry." *Chemical Geology* 144(3-4): 269-280.
- Pearson, N. J., O. Alard, et al. (2002). "In situ measurement of Re-Os isotopes in mantle sulfides by laser ablation multicollector-inductively coupled plasma mass spectrometry: Analytical methods and preliminary results." *Geochimica et Cosmochimica Acta* 66: 1037-1050.

Pb

Reference:

- Collerson, K. D., B. S. Kamber, et al. (2002). "Applications of accurate, high precision Pb isotope ratio measurement by multi-collector ICP-MS." *Chemical Geology* 188: 65-83.
- Doucelance, R. and G. Manhès (2001). "Reevaluation of precise lead isotope measurements by thermal ionization mass spectrometry: comparison with determinations by plasma source mass spectrometry." *Chemical geology* 176: 361-377.
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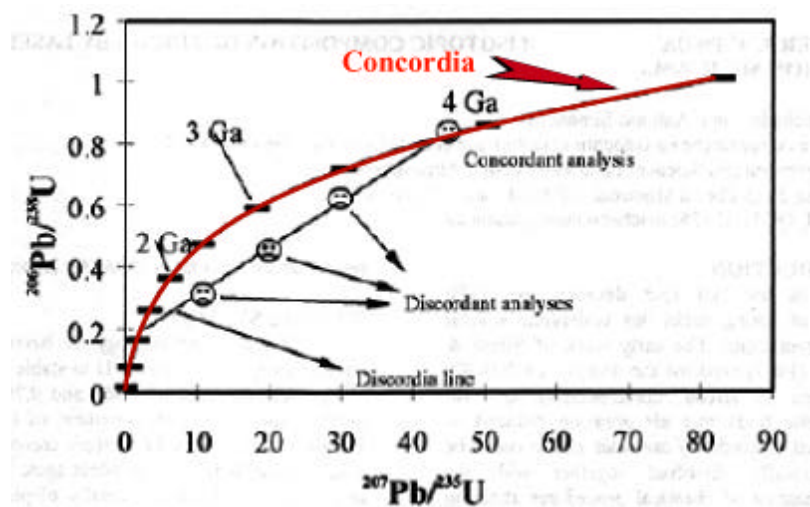


Figure 5_1: The principle of the concordia diagram (from Machado and Simonetti, 2001)

U-Pb

The U-Pb system is an important geochronological tool.

Two isotopes of U decay to Pb with very different half-lives. Therefore chemical processes will not change the ratio of the two U isotopes to each other and will not change the ratio of the two Pb daughter isotopes to each other.

$$\text{Pb}^{207} = \text{U}^{235} (e^{\lambda_1 t} - 1)$$

$$\text{Pb}^{206} = \text{U}^{238} (e^{\lambda_2 t} - 1)$$

Zircon is relatively insensitive to geological processes such as chemical alteration, erosion, sedimentation, metamorphism, anatexis, and is a ubiquitous accessory mineral in magmatic rocks. Recent analytical developments have demonstrated the benefits taken from the geochemical and isotopic information provided by the ubiquitous and magmatic zircon phase. Over the last few years, different groups have successfully used LA-(MC)-ICP-MS for the in-situ determination of U-Pb isotopic measurement in zircon (Thirlwall & Walder 1995, Hirata & Nesbit 1995, Machado et al. 1996, Scott & Gauthier 1996, Fernandez-Suarez et al. 2000, Hirata 1997, Horn et al. 2000, Ballard et al. 2001, Bruguier et al. 2001, Ketchum et al. 2001, Knudsen et al. 2001, Li et al. 2001, Machado & Simonetti 2001, Kosler et al. 2002). Some of these work have focussed on the sedimentary provenance of the zircon (Machado et al. 1996, Scott & Gauthier 1996, Fernandez-Suarez et al. 2000, Ketchum et al. 2001, Kosler et al. 2002, Hidaka et al. 2002). Previous studies (Morton et al. 1996, Fernandez-Suarez et al. 2000) have shown in particular that, in order to isolate a major sedimentary source component, it is required to analyse a large number of samples. LA-ICP-MS is the method of choice on a timely and cost effective basis in comparison with other conventional dating technique for zircon age dating of Proterozoic and Archean rocks. Using quadrupole based instrument, recent studies have shown that, with the proper error propagation, the precision of U-Pb age is only slightly worse than SIMS-based ion probe dating (Horn et al, 2000; Kosler et al, 2002). Similar or better errors are expected using magnetic sector ICP-MS because of a better ion transmission and peak shape. However the error in U-Pb zircon age determination is related to (1) U-Pb fractionation during the ablation process (2) the ability to accurately correct for the mass bias induced by the ICP source (3) the ability to measure Pb204 and correct for common lead.

(1) U-Pb fractionation:

- particle and laser wavelength dependant
- rastering vs. single spot
- defocusing conditions
- mathematical corrections
- active focussing
- He atmosphere

(2) Kosler et al (2001) mixed the ablated sample with mixed desolvated solution of ²³³U enriched and thallium using an AridusTM. Horn et al (2000) prefer using ²³⁵U instead of ²³³U but in this case a correction for natural ²³⁵U is necessary.

Kosler et al (2001) technique summary:

- Monitor Hg202, Pb204-206-207-208, Tl203-205, U233-235-238 (monitor ²³²Th for Th enriched samples such as monazite for ²³²Th-²⁰⁸Pb decay scheme)
- Used mixed Ar-He gas in the sample cell later on mixed again with 10ppb Tl and ²³³U
- Raster a 40*40 µm square on your zircon, while defocus the beam, for 60s.
- Use higher sample time (dwell time) for isotopes such as Pb204-207 because of their low count rate
- Scan as fast as possible (lower settling time) and acquire data
- Correct all data for dead time
- Correct for the mass bias using ²³⁵U/²³⁸U
- Correct for remaining Pb/U fractionation using a least square linear regression

$$R = R_0 + ST$$

R = isotopic ratio

R_0 = intercept value

S = slope

T = laser ablation time

R_0 is calculated using the following equation:

$$R_0 = \frac{\sum r_i - \frac{\sum t_i \sum r_i}{\sum t_i}}{n - \frac{(\sum t_i)^2}{\sum t_i}}$$

'n = number of isotope ratio

t_i and r_i are individual time and isotopic ratio

The uncertainty associated to the fractionation-correction ratio could be calculated using the following equation:

$$\sigma_{R(1c)} = R_{1c} \sqrt{\frac{\sigma_{R(1m)}^2}{R_{1m}^2} + \left(\frac{M_1}{M_2}\right)^2 * \frac{\sigma_{R(2m)}^2}{R_{2m}^2}}$$

U series

U-Th

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ID

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