Eidgenössische Technische Hochschule Zürich
Ecole polytechnique fédérale de Zurich
Politecnico federale di Zurigo
Swiss Federal Institute of Technology Zurich

Institut für Mineralogie und Petrographie

Preparation of glass beads and powder pills for XRF analysis of silicic and calcareous rocks

(standard version)

- Edition 2000 -

Volker Dietrich and Florian Schwandner
Institute of Mineralogy and Petrography, ETH Zürich

Use of the analytical facilities (including preparation labs and machines) of ETH-IMP for a PhD or Diplom thesis requires successful participation of the ETH course "Physikalische Methoden der Mineral- und Gesteinsanalyse".

ROCK SAMPLE ANALYSIS

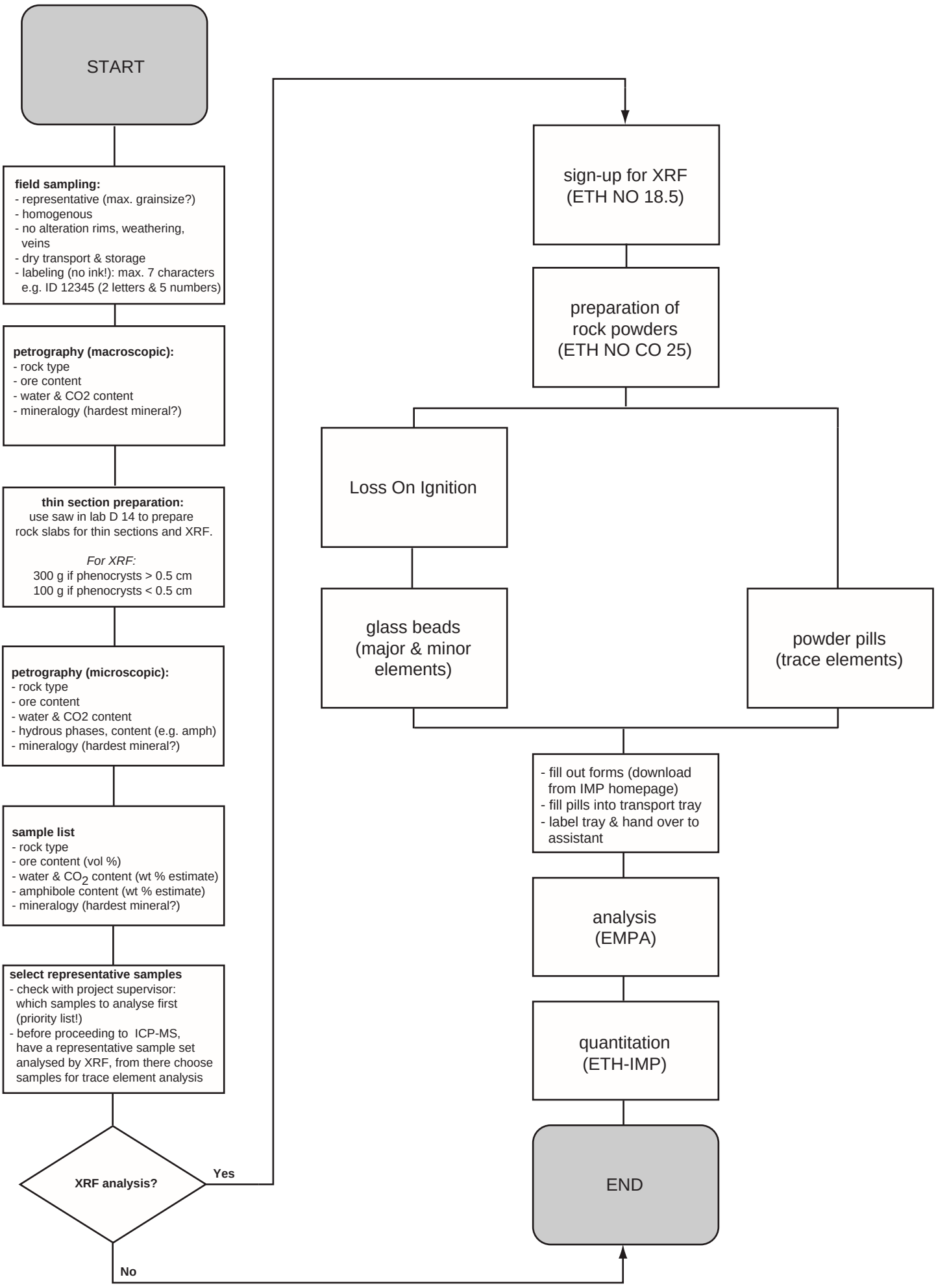

Table of contents

For publication/thesis:

Methods of preparation and calibration in:
Nisbet et al. (1979)
Dietrich et al. (1984).

Nisbet, E.G., Dietrich, V.J., and Esenwein, A. (1979). Routine trace element determination in silicate minerals and rocks by X-Ray Fluorescence. *Fortschr. Mineral*., **57** (2): 264-279.

Dietrich, V.J., Carman, M.F., Wyttenbach, A. And McKee, E.H. (1984). Geochemistry of basalts from Holes 519A, 520, 522B, and 524, Deep Sea Drilling Project Leg 73 (South Atlantic). *Init. Reports DSDP*, **7**: 579-601.

Reusser, E. (2000). XRF 2000. *ETHZ-IMP Internal Report*. [data treatment software]

Regulations

- ***Every*** **user has to register beforehand, without exception** (on calendar in E 18, key for NO CO 25 and platinum crucibles from the assistant). By signing up, full responsibility is taken and the rules, operating instructions and safety rules of ETH are accepted.

- **Each user has to fully report in the lab journal (with assistant) after work period is completed.**
  A sample is given on the first page of the lab journal. The points to note are:

> **readable** name/institute/tel.-no. or e-mail date
>
> work (XRF: powder pellets or glass beads, which program and how many spls)
> (crushing: jaw breaker, hydraulic press, or (which) mills and how many spls)
>
> rock types (exotica ?)
>
> incidents/notes
>
> *always do and note:*
> cleaned up, consumeables refilled, cleaned
> platinum crucibles and keys back
>
> signature

Sample identification: maximum of 7 figures: 2 letters & 5 digits (e.g. FS 12345).
Other formats are not allowed and can not be considered for analysis. The data acquisition and treatment software accept only this format.

No samples will be sent to EMPA for analysis, if the following conditions are not fulfilled:
- sign-out is incomplete or missing,
- the lab is not left in good condition,
- the lists (forms) are not readable (print or fill out on computer).

- The devices and their **settings must not be modified.**
  Working on weekends and at night requires prior approval of the assistant.

- **Preconditions for use of the lab** are the successful visit of the course “Physikalische Methoden der Mineral- und Gesteinsanalyse” and a personal instruction by the assistant.

V.Dietrich/Assistenten

For any questions please contact the lab assistant Andreas Häfner, NO. E 18.5
(E-mail: haefner@erdw.ethz.ch, (Tel.: 27802)

1 rock specimen preparation

The following instructions apply to silicate and carbonate rocks. Production of pills from non-silicate (or carbonate) rocks without prior approval and instruction of the laboratory leader results not only in significantly more work (preparation, measurement, interpretation) but also results into errors of the instruments and of the final results. Non-observance can result into exclusion from laboratory work and possible compensation payments. This is especially the case for rocks with an ore content >5% (esp. sulfidic), sulfates, slags and flint.

sample selection

The sample/specimen should be fist-sized, about 200-500 g, and shouldn't have any veins, paint (sample numbers etc.), grease from the saw, or weathered sections.
We advise to group samples of similar composition and to treat them groupwise. This reduces the probability of contamination! (see p. 8) Setting up of a sample list with priority assignment is strongly recommended:

- own name, exact sampling location, date, unit, etc; representative for what? use/scientific question?
- field description (rock type), macroscopic classification
- microscopische description (texture, mineral content, rock type)
- amphibole content, ore content (sulfidic, oxidic?), approx.content of hydrous minerals
- sample ID (**alphanumeric, no symbols, max. 7 digits**) and relative priority

1.1 Backenbrecher & Hydraulikpresse (rock crusher & hydraulic press, NO CO 25)

Backenbrecher : use for large samples, only. Crush the clean sample and use a hand magnet to remove metal splinters or fragments (contamination!).

hydraulic press : use for normal to small sized samples. Place isometric cut pieces or grains of maximum diameter of 20 mm on the anvil. Crush them to 1-2 mm-sized grains.

Caution! Both devices should be cleaned using the air hose and acetone. *Do not* use water! Rust leads to elevated Fe, Ni & Cr values!

1.2 Homogenize sample

Powder sized sample grains of equal size but different density will vertically separate if you only tap the jar on the table too hard. Inhomogeneities and unknowingly wrong or not at all interpretable results follow.

1.2.1 Probenteiler ("fair split")
Fair-split and reunite the crushed sample several times: on white printing or wax paper, separate a symmetric pile of the powder into four sections, using a spatula. Re-unite facing quarters in diagonal direction.

1.2.2 Stechprobe (piece out method)
Piece out a fraction of the sample from a sample cone using a tube end (1.5 – 3 cm diameter, bring your own; alternative to 1.2.1)

1.2.3 Schütteln (shaking)
Shake the sample well, in a plastic bag or pot, together with two agate balls, by rotation & excentric shaking over a horizontal axis (homogenizing!).

1.3 disk mills ("Sacheibenschwingmühlen", for grinding gravel to powder)

1.3.1 large thungsten carbide (WC) shatterbox (Wolframkarbid-Mahlgefäss, gross)

Caution! NEVER knock any of the pieces of the tungsten carbide (WC) shatterbox together - they will very probably brake! The material is *very* brittle and expensive. Under no circumstances attempt to grind chert (flint), the mechanic treatment pyrolizes (strongly exothermic) the organic content, and the disk cylinder breaks to bits.
Control before grinding: are the mobile interior parts (rings and central disk cylinder) of the shatterbox actually mobile? Are no sample residues on or beneath the rubber ring?
Is the sealing ring in the lid placed right? Is the lever handle actually in entirely closed position?

Grind on setting 2 (high rotational velocity).

grind with large shatterbox:	**ideal amount of sample (g)**	**time (minutes)**
quartz-rich rocks: granite, granodiorite, quartzite, etc.	60	4
greenschist, serpentinites, basalts	60	5
eclogites, garnet-rich rocks	60	6

grind with small shatterbox:	**ideal amount of sample (g)**	**time (minutes)**
quartz-rich rocks: granite, granodiorite, quartzite, etc.	20	2
greenschist, serpentinites, basalts	20	3
eclogites, garnet-rich rocks	20	5

1.3.2 Agate (Achat) shatterbox

(only for ultrapure sample preparation, as for ppt-range analyses, e.g., trace elements in ultramafic rocks)
A maximum of 30 g sample may be ground for app. 5 minutes (depending on rock type). **Use setting 1, only! (slow velocity)**

Homogenize the sample after the grinding. Fill them in sample containers, but don't shake them, they will dehomogenize again.

Cleaning of the shatterbox: use warm water, dry, then acetone. The outer steel rusts easily!

1.4 Contamination effects through grinding

The following Information should be taken serious when attempting to grind rocks in the XRF sample preparation lab CO 25. For any questions, contact the lab assistant.

Note: The greatest systematic errors through contamination occur during rock crushing and grinding, not in later wet chemical digestion or analytical procedures! For powder pills, grain size must not be greater than 64 micrometers (a sieve with 250 mesh without residues). If the powders feels and looks like flower when rubbing between your fingertips (no grains felt), then the powder is right.

1.4.1 oxidation effect.

When grinding rock pieces, Fe (II) -bearing minerals heat up and react with atmospheric O_2. To critically evaluate the effect on your sample, you might consider two ideas:

- treat all your samples the same way too keep the systematic error to the same level. This makes your results more reproducible, precise and comparable. For example, always use the same mortar of the disk mill for your samples, use the same amount of sample, and the same grinding time (if equality of composition allows it, see lab manual for composition-time relation).
- Seperately determine FeO by spectrophotometry (contact V. Dietrich) on coarser powder. J. POTTS (1987) reports up to 20% increase of Fe_2O_3 relative to FeO in the same sample allready, when grinding for less than 10 minutes!

1.4.2 Contamination through mortar material

Different mortar materials cause different contaminations. the best systematic study was done by THOMPSON & BANKSTON (1970). They compared different mortar and sieve materials by grinding high purity quartz. Some of their results are listed below:

grinding equipment	**contaminating element**	**concentrations in SiO2 test sample**	**concentrations in SiO2 test sample**
		Batch 1(ppm)	**Batch 2 (ppm)**
Tungsten Carbide	Co	32	8.6
	Ti	124	102
	Ta	5	5
	W	n.d.	n.d.
Al-ceramic	Al	> 2000	> 2000
	Cu	2.6	2.0
	Fe	34	55
	Ga	21	54
	Li	1	1
	Ti	11	31
	Zn	2.9	<2
Agate	B	1.8	2.3
	Cu	1.1	3.9
	Si	n.d.	n.d.

Other useful references with similar data can be found in JOHNSON & MAXWELL (1981), p. 75, BENNET & REED (1971), p. 10ff, and in ZIEF & MITCHELL (1976), p.153.
In addition, especially Nd and Ta among other HFSE (high field strength elements) may show contamination by using thungsten carbide.

1.4.3 Cross-contamination effects

Cross contamination means: Contamination of sample B by traces of sample A, when sample B is ground after sample A, using the same container. This is probably the greatest contamination effect. To avoid or minimize this effect, consider two ideas:

- Carefully read and follow the lab manual instructions for cleaning the equipment. Rather run the mill with quartz twice than only once between samples. Note: cleaning the mortar with water, and aceton after (see manual) carefully and running it once with quartz can give better results than loosely cleaning it but running with quartz twice.
- Think of the right order of grinding your samples. Similar compositions give less contamination.

There is actually a *reason* why certain mortars are assigned to certain rock chemistries!

1.4.4 Literature

POTTS, J. (1987). *A handbook of silicate rock analysis*. Blackie London, 622pp.

JOHNSON, W. M., & MAXWELL, J. A. (1981). *Rock and Mineral analysis*. Chemical analysis series Vol. 47. J.Wiley, New York, 489 pp. (2nd ed.)

ZIEF, M., & MITCHELL, J. W. (1976). *Contamination control in trace element analysis*. Chemical analysis series Vol. 47. J.Wiley, New York, 262 pp.

BENNET, H., & REED, R. A. (1971). *Chemical methods of silicate analysis*. British Ceramic Research Association. Academic Press, London, 272 pp.

THOMPSON, G., & BANKSTON, D.C. (1970): Sampling contamination for grinding and sieving determined by emisssion spectroscopy. *Appl. Spectrosc*. **24**:210-219.

2. Preparation of powder pills for trace element determination

powder pills are produced by pressing the rock powder under a maximum pressure of 450 bar. Before pressing, an acrylic polymer resin is added in order to have the individual grains stick together.
It is dissolved in acetone (polymerizes quickly in water), which vaporizes and leaves a grain-coated coagulate of grains behind. Under pressure, it flows into one mass and binds the grains together. Once the pressure is released, it solidifies and the result is a solid pill that can easily be measured in the XRF spectrometer. An earlier version used polyvinyl alcohol instead (much more toxic). Make sure to have read the MSDS before using it.

Procedure:

1. Dry the powder overnight in an oven at 110°C.

2. Weigh ca. 10 g dry powder in a 150 ml beaker.
3. Add a 2/3 pipette of 10% Elvacite (dissolved in acetone).
4. With a thick glass rod, stir until the powder appears to dust out of the beaker
5. Repeat twice, then add 1/3 pipette and repeat twice. Total: 2.3 pipettes (2 mL)

6. Fill the dry powder into the pressing equipment, don't stir, but distribute equally while pouring. Make sure the piston is right side up (polished side down)
7. Insert equipment into hydraulic press and apply pressure (350 to 450 bar).
8. Leave for one minute, NOT longer!.
9. Release pressure ***slowly*** by opening the release handle.

10. Securely grab the device at bottom and top, turn upside down slowly, secure piston.
11. Take bottom plate off. Careful: don't drop piston. Cover cylinder piece bottom with plastic cap. Turn right side up again and re-insert into hydraulic press.
12. Slowly, by hand, press the piston down into the cylinder to press the pill out of it and into the plastic cup (press by turning the top wheel of the press). Hold the piston with two fingers while doing so (you feel it releasing), and stop applying pressure as soon as the pill is released, otherwise it will break.
13. Remove assembly and carefully drop the pill onto a clean paper towel.

CRASH-TEST: The pill gets dropped onto a stainless steel surface inside the x-ray spectrometer and may brake if it was not made well. To simulate and test it's behaviour, drop it from 8 cm hight on a double paper towel. It should neither break nor have cracks. If so, grind it in the agate mortar/pestle and add another 1/3 mL Elvacite, try again.
We perform crash tests with some of the the pills to ensure that they were tested. If a pill breaks in the XRF spectrometer, it has to be taken apart and cleaned which takes ½ day.

DO *NOT* TOUCH PILL SURFACES WITH YOUR FINGERS!!

3 Preparation of Glass Beads for Major Element Determination

3.1 Determination of the Loss on Ignition (L.O.I.)

Material:

weighing:

ceramic crucible (glass cupboard)
powder spatula (drawer)
dried sample powders in jars
acetone, Kimwipes
form „L.O.I.“

ignition

- heated oven (Muffelofen)
- long tongs
- large leather gloves
- small Nomex® gloves (densely woven cotton)
- protection glasses with light filter
- fiber ceramic plate
- dessicator with blue drying agent (if it appears pink, it has to be placed into the drying oven for dehydration, in the large ceramic bowl)

3.1.1 drying and using the oven

Let the sample dry in its sample glass bottle, without the lid, in the oven for 6 hours (best overnight) at 105-110°C in order to remove remaining moisture (in earlier times called H_2O^-). The oven has to be pre-heated. On maximum heating rate, it takes about 2 h. Is it switched off, any temperature programming may be lost. Note that the display is in minutes. Some users prefer to program it the night before, so that they can start using it right away once they arrive in the morning.

3.1.2 sample amount

1.1 g sample powder for normal silicate rocks (L.O.I. of 1-10 wt.-%),
1.2 g sample powder for chlorite-rich or serpentinitic rocks (L.O.I. of 10-20 wt.-%),
1.5 g sample powder for carbonaceous rocks (L.O.I. of 30-50 wt.-%).

Weigh the empty ceramic crucible exactly and note the mass (n_1) on the LOI form. Slowly add the powder and weigh and note the total mass (n_2 = ceramic crucible + sample powder). The point is not to exactly hit the right mass of sample but to determine it with an accuracy of 0.1 mg.

3.1.3 burning-off

Place the crucibles (numbered at bottom) into the oven and burn them red-hot at least 1 hour at 1050°C (1070°C if amphibolees >5%vol). Take the crucibles out and place them onto the fibre ceramic plate (at the Bunsen burner). After 5 minutes it is cold enough to handle it with a Nomex®-glove. This protects your fingers and ensures that no skin fat or tissue is stuck to the crucible which would contribute to the error of the weighing result, and place it into the dessicator.

3.1.4 calculate L.O.I.

Weigh the crucible cold, always 10 minutes after removing it from the oven. If it was still too hot it would heat the air in the closed weighing chamber which would expand and press on the scale. Room temperature is reached in the crucible after ca. 5 minutes. In experiments performed in this lab, it became obvious that the error due to adsorption of air moisture becomes negligible after 10 minutes. After 15 to 20 minutes though, recarbonatization plays an increasingly significant role. Note its total mass (n_3) and calculate the L.O.I. :

Formula for L.O.I. :

$$\text{L.O.I. (weight \%)} = 100 \times \left((n_2-n_3) / (n_2-n_1) \right)$$

The L.O.I. is made of contributions from:

Volatile compounds:	H_2O^+, CO_2, F, Cl, S; in parts also K, Na (if heated for too long);
Hinzugenommene Anteile:	O_2 (oxidation, e.g. FeO to Fe_2O_3), later CO_2 (CaO to $CaCO_3$).

NOTE: For later interpretation of the results of measurement: Due to the escape of volatiles, there will be an increase of mass among all other oxides. By oxidizing FeO to Fe_2O_3, the value of $Fe_2O_{3\ total}$ increases but all other oxides will be mass-reduced. These changes in concentration are considered in the calculation of the analysis.

3.1.4 Rehomogenization

If necessary (suggested), rehomogenize the burned off sample in an agate mortar. Depending on rock chemistry, at 1050° C and following cooling, a sintering, partial glass formation, or partial crystallization might occur. The grinding of the sinter optimizes the homogeneity (**frequent source of error!!**)

3.2 Casting glass beads

Instruction manual Perl 'X3 - Automated glass bead casting machine -

3.2.1 The Machine

The Perl 'X3 casts glass beads in standardized dimension in a single automated procedure. The casting powder (mixture of sample and flux) is rapidly heated in a high frequency induction furnace. An automated agitation device homogenizes the material and removes gas bubbles from the melt. The actual casting is isothermal, casting dish and crucible are held at the same temperature. This prevents crystallization of the sample. Vitreous solidification of the melt is done with pressurized air cooling.

The whole process takes 6-7 minutes depending on the program chosen. The machine can be used again immediately after a run. The product can be analysed directly; no subsequent polishing is necessary.

3.2.2 Preparation of casting powders

The casting powder is a homogenous mixture of the sample powder dehydrated by ignition and a flux ($Li_2B_4O_7$ – di-lithium tetraborate). The flux lowers the melting point of the mixture far enough, so that the powder easily melts at ca. 1150°C and can be casted.

1 g of the sample powder dehydrated by ignition is to be weighed on weighing paper or in a small glass beaker. Then 5 g dilithium tetraborate are added. These masses have to be accurate by four digits (1.0000 g). This ensures an exact mixture of 5 : 1 (flux : powder), necessary for calibration to the internal standard Li.
The powder is transferred quantitatively into an agate mortar and homogenized with the pestle. Coarser grains of the ignition-dehydrated powder will also be ground in this process. Homogenisation is necessary because the agitation in the furnace alone still results into measurable inhomogeneities and thus to larger analytical errors. As long as the powder is not absolutely homogenous, any spilling of powder over the mortar rim will alter the analytical result.

The scale: Never switch the scale off, also not overnight or on weekends. The weighing will also be much more stable. If the indicated masses seem unstable, recalibrate the scale as follows:

Operational steps:

1. Close the sliding doors; check the bubble in the level ring and adjust level on the scale feet, if necessary.
2. Hold black key down until the display shows 'CAL ----', then release. The scale begins auto calibration. After a while the figure 100.000 is displayed (blinking).
3. Slowly push the black lever on the right hand lower rim of the back away from you. This sets the calibration standard mass onto the weighing lever. After a while, the figure 100.000 is displayed constantly (not blinking), and then the figure 0.0000 blinks.
4. Slowly pull black lever back to front. The scale will return to its original display.

The powder mixture has to be transferred quantitatively into the Ti crucible after homogenisation. Please ensure that no powder is on the flat rim of the crucible. Remove with towel or rubber spatula - the powder can interfere with the casting.

3.2.3 Casting with Perl ’X3

3.2.3.1 Start-up and operation

The machine must never be loaded with more than 6 g total mass (powder + flux). Otherwise the melt will overflow upon casting and the machine will be damaged. In the most fortunate case one only gets an inhomogeneous glass bead.

Operation of the machine is done through simple menus on the display of the operation microprocessor.

a. Make sure that the ultrasonicator bath is filled with water (level up to 3 cm below rim, see mark) and plugged in.
b. Switch cooling water OUT (“Rücklauf”) all the way on, then switch IN (Vorlauf) on, at last switch pressurized air on. Now turn back cooling water IN by ½ turn.
c. Switch the additional air pump on the exhaust pipe behind the machine on (switch #1: transformer on lab bench; switch #2: on separate power line), open valve on exhaust pipe (pull, then turn).
d. Open vertical front cover of the Perl X3 and check fuses.
e. On the operation unit, press 'ON'.

On the display, 'WAIT...' is shown (self test is being conducted). After this, 'SEARCH FOR VERTICAL POSITION....' is displayed, indicating the automated calibration procedure for the setting of the agitation unit. Machine cover and crucible lid open automatically.
The Perl X3 now conducts a self-test of the electronics and the supply lines (cooling water and air) after the start-up. If the settings do not meet the requirements, the start of the machine will be interrupted automatically. The operation microprocessor gives an error message (for how to get out of the error menu- see below).
In such a case, please first check if cooling water und pressurized air valves are on. In any case, restart the machine after this. It may happen that the pressure in the cooling water lines is momentarily unstable. If this does not help, stop working and indicate the error to the lab assistant.

3.2.3.2 The Menu and available programs

After start-up, a total of three main menu pages with different submenus can be used. Move between the pages with the ▲ and ▼ buttons.
Operate as follows: press ▼ button until the second main page is displayed:

PROGRAMMING [1]	COOLING [6]	SELECT [2]
DISH[3]	CRUCIBLE LID [4]	COVER [5]

The menu options 'Crucible Lid' and 'Cover' ([4] and [5]) open and close the covers/lids. 'Dish' ([3]) changes the casting dish position (turn by 180°, vertical axis). 'Cooling' ([6]) activates/deactivates the pressured air-cooling of the casting dish. Only authorized persons can use the menu option ‘Programming’ which is password secured.

The menu options on the third main menu page ('Dish [1] or [2]'; 'RS232'; 'Delete Program'; 'Fusion Counter') are not of any use for the 'normal' user. They are only being used for programming and maintenance purposes. Do not change any settings in this menu.

To choose the desired program:

Activate the 'SELECT' ([2]) function by pressing the number 2 key on the keyboard. You will be prompted to enter a program number. Press the corresponding program number (see below) and then 'ENTER'. The operation microprocessor automatically displays the first (main) menu page again

SELECT PROGRAM : 4 START SELECTED PROGRAM [START]

After the words 'Select Program', the last used program number is displayed (in the above case, #4). For glass bead casting, four programs are currently programmed:

program No. 4	basaltoids
program No. 5	ultramafitites
program No. 6	syenites, granitoids
program No. 10	carbonates, calc-silicate rocks

If you want to cast different rock compositions, you must seek advice with the lab assistant first. Before using the carbonate program, you must also consult the lab assistant. The following materials are **not allowed** for processing:

- ***NO*** **slags und cinders (e.g., flying ashes)**
- ***NO*** **ores (especially sulphides)**
- ***NO*** **sulphates**

Use of these materials lead to partial destruction of the platinum dish and crucible. A separate preparation protocol for rocks with oxidic ore content >3%vol (dilution with standardized quartz powder) exists and has to be individually assigned by the lab assistant. No guarantee can be given for its success.

3.2.3.3 Activation of a casting program

Place the crucible containing the powder into its holder. Take care when placing it: the holder is extremely hot if the machine has just been used before. Always use the special crucible tongs but ***never*** **let the tongs touch the inside or upper rim of the crucible**! Only touch the outside. Melt drops will be almost impossible to remove from scratches and will contaminate further samples.

With the same tongs, touch the casting dish on the rim only, but never on the casting surface. Any scratches will be on the glass bead measurement surface also, and will cause the incident X-Ray beam to be out of focus. Open the front dish holder with one hand (can be hot) and place the dish into position. The upper notch of the three holder pins is where the dish goes. Make sure the holder encloses the dish safely. The machine will rotate the dish into casting position after start of a program. Choose the desired program (menu option 'Select') and then press the yellow 'Start' Button on the upper front of the machine. From here on, everything is automated.

During operation, the main individual program steps can be read from the display:

PGM: *(number)*	*(program step)*	
T: *(mm:ss)*	TR: *(mm:ss)*	Temp.: *(number)*°C

PGM indicates the number of the active program, followed by display of the program step conducted ('First Fusion', 'Second Fusion' etc.). **T** indicates the remaining time until completion of the active program step, **TR** that of the entire program with subsequent air-cooling. **Temp** shows the current temperature on the crucible outer wall by optical measurement with an infrared pyrometer. It is not possible to measure temperatures below 550 °C with this device; the machine displays this as *<550 °C*.

3.2.3.4 Sequence of events during casting

The currently available programs comprise the following steps:

a. *First Fusion:* melting of the powder with agitation – depending on program at 1050 - 1150°C (duration 3 - 3.5 minutes).
b. *Second Fusion:* Homogenisation of the powder at 50°C higher temperatures than in the first step (duration in most cases 2 minutes).
c. *Pause before Casting:* The crucible is tilted by about 30° to allow the melt to accumulate in one corner of the crucible. In case of ultramafics, the temperature rises once more by 30°C. *[It is sometimes possible that an error occurs and the machine stops the program. In this case, shut down, restart entire program without removing crucible or call lab assistant]*
d. *Casting:* crucible abruptly tilts into a 140° position and empties the melt into the casting dish. During this step, the machine beeps once a second (signal, can not be switched off). The melt should immediately cover the entire casting dish floor. *[If a fast beeping occurs after casting, an error message is displayed. Press ▲ twice after about 10 seconds, then press ENTER. From the menu, press 3 on the keyboard (DISH) to rotate dish holder to front position. Press 6 on the keyboard to manually activate air-cooling, press 6 again after one minute to switch cooling off. Press 5 on keyboard to open cover and remove dish with glass bead as normal] See also error messages/trouble shooting section.*
e. *Pause for Solidification:* Heating of crucible and casting dish is switched off and the induction coils are internally cooled with water. This ensures an abrupt temperature drop in the melt to increase viscosity. This is necessary so that the melt doesn't deform during rotation of the dish to the front position for forced air-cooling.
f. *Forced Air Cooling:* The casting dish holder rotates the dish to the front position. Forced air-cooling for one minute is vitrifies the melt and the resulting glass bead detaches from the dish by itself.
g. *Handling after program:* In the same moment that air cooling starts, the crucible holder rotates back to vertical position and the cover and crucible lid open. As soon as the hot crucible is accessible, carefully remove it from the holder with the tongs (hold it on the outside only! There are two gaps in the ceramic crucible holder on either side for this purpose) and place it into the ultrasonic bath. By doing so, only minimal glass remnants stay in the crucible.
   As soon as the forced air-cooling is shut off, the program is finished and the casting dish can be removed with the tongs. The machine is ready for a new run.
   Never touch the slightly convex side of the glass bead with your fingers. You will experience elevated sodium values in your analysis. If it occurs, gently wipe the surface with a soft Kimwipe with alcohol.

It is possible to program and operate the machine so that glass beads can be produced without interruption (i.e., the new casting process starts while the prior glass bead is still being air cooled). This requires an additional programming step that can be utilized by experienced users upon request from the lab assistant, provided a second casting dish is available and the machine runs trouble-free.

Please be cautious that **no new casting process is to be started while the old glass bead is accidentally still in the casting dish**. If this is the case and a new melt is being poured, then the melt will spill over the rim of the casting dish and will damage the machine. In case of a program begun with a still remaining glass bead in the dish, just shut off the machine during the program with the red OFF button. The machine does not have a spill auto-shut-off.

3.3 Cleaning and proper treatment of the platinum material

For use of the machine, one casting dish and several crucibles are handed out to the user. This is to ensure a continuous use of the machine.

During run of a program, the last used crucible is placed in warm (not boiling, ca. 80°C) hydrochloric acid (HCl 5%). 5 minutes are enough to clean the crucible if it has been temperature-shocked properly in the ultrasonicator bath. A hot plate (set dial to 6), glass beaker and acid are in the lab.
Under normal conditions of use, the casting dish doesn't have to be cleaned by this procedure. It is only placed into the acid after the last sample for a few minutes.
This is mainly to keep the lower side of the dish clean and reflective. The rotation of the dish holder from the cooling to the casting position and back, the casting dish temperature and the detection if a dish is in the holder is by an optical sensor that requires reflection on the lower side of the dish.
Never place the dish into the acid bath together with the crucibles! Their rims would scratch the inner casting surface of the dish.
If the room is left for any short time, switch the hot plate off and leave the platinum in the acid bath. Switch the main gas supply off if you leave the room (in door frame, red button = OFF).

Waste acid has to be poured into the white 10 L waste acid container next to the sink. Place container into the sink, unscrew top, pour waste acid in (***GLOVES, SAFETY GOGGLES, LAB COAT!!!***). If the container filling reaches the marked top level (ca. 10 cm below top), inform lab assistant for proper disposal. Do not pour waste acid into the sink. ***NEVER*** **pour water into the waste acid container, explosion hazard!**

Under no circumstances are the inner parts of the crucible or the casting dish ever to be touched by the tongs!! Even slightest contacts scratch the platinum surface. On these scratches, small melt drops remain, leading to lesser quality melts and contaminated glass beads. The platinum crucibles and/or dish would have to be replaced which takes about a month and is extremely expensive (ca. 5000, - CHF per item!).

After extensive use, the casting dish will deform to leave a convex surface on the analytical side of the glass bead. Scratches and uneven surface can be flattened and polished by about 4 hours work. Uneven surface leads to a defocused incident beam during analysis.

3.4 Troubleshooting and Error messages

3.4.1 Casting problems

Even though the machine is in use since 1996, casting problems may still occur. The experience of the last years led to many sometimes-funny incidents and improvements in this current protocol. Please always notify the lab assistant if obvious errors occur, so that further improvements can be implemented in the future.

a. *The bead does not cover the entire floor of the casting dish*:

a1: The bead was casted a few degrees too cold. Occurs with ultramafitites (dunites) and rhyolites. Solution for rhyolite: make new powder mixture and cast with program No. 4. A solution for dunitic chemistry could possibly be dilution with a quartz standard but this procedure is currently in the testing stage.

a2: You may observe a darker glowing colour of the casting dish at the corner that is not covered by the melt. In that case, stop all operation and contact the lab assistant for maintenance. If the glowing colour is uniform, the melt is too viscous and the wrong program was chosen.

b. *Small melt remnants stay behind in the crucibl*e:

If the acid bath is too slow, either the acid is saturated with metals and thus won't dissolve the glass (change acid), or the solubility of the particular sample glass is too low (e.g., often with high ore content). In that case, melt 6 g (under no circumstances more!) pure di-lithium tetraborate in it. Cast with program No. 4. The bead won't detach as easily from the casting dish. Very carefully, tap the rim of the dish on a lab bench.

c. *The bead has a small gas bubble trapped in its rim*:

The bubble won't change the quality of the analysis, because the outer millimeters of the bead are not incorporated into the measurement grid. Treat the dish for 5-10 minutes in warm acid.

d. *The machine turns itself off without error message*:

A fuse might have popped out. This doesn't happen as frequently anymore, since a separate power line was installed. This error sometimes occurs directly after start-up of the machine. During the initial internal system check, the high frequency generator for the heating coils is switched to maximum power. This does not happen during a normal run at the temperatures used in the current programs.

3.4.2 Maintenance checks

Three maintenance checks are usually employed once a month or after the machine has not been in use for more than a day:

DISH DETECTOR TEST

Try running a program (e.g., #4) with a crucible, without sample, but without a dish. The program should abort automatically after a few seconds. It should give the error message NO DISH.

WATER FLOW TEST

Try running a program (e.g., #4) with a crucible, without sample, with a dish, but shut the water off. The program should abort automatically after a few seconds. It should give the error message WATER FLOW ERROR

AIR FLOW TEST

Try running a program (e.g., #4) with a crucible, without sample, with a dish, but shut the water off. The program should abort automatically after a few seconds. It should give the appropriate error message.

3.4.3 Error Messages

The machine gives clear error messages. All operations are automatically stopped if this happens. Is the source of the fault detected and removed, the machine can be brought back to normal operation mode by pressing the ▲ key twice, then the ENTER key.

Possible error messages and what you could do:

FURNANCE COVER POSITION FAULT E1

Furnace cover is in wrong position.
Help: turn pressurized air on all the way.

CRUCIBLE COVER POSITION FAULT E3

See above.

WATER FLOW ERROR E14

Pressure of *cooling water in* (Kühlwasserzufluss) too high or too low.
Help: check if IN and OUT are all the way open. If this doesn't help, inform lab assistant.
The machine will abort all operations if this error occurs during run of a program. The melt can be recovered or casted by restarting the program again. The resulting glass bead has to be discarded though, because inhomogeneities and mass fractionation of certain light elements will become significant.

NO DISH

The optical sensor does not detect the casting dish. Place casting dish in either one of the two dish holders. If a dish was present, either the sensor is defect or the lower side of the dish is not reflective anymore. In that case, treat the dish for 5 minutes in the acid bath, rinse and dry, insert, and restart. In the case of repeated occurrence of this error message, inform the lab assistant.

CRUCIBLE POSITION FAULT

The crucible holder assembly does not find the vertical position. Turn off machine, wait 20 seconds and restart. In the case of repeated occurrence of this error message, inform the lab assistant.

3.5. Casting Glass beads by hand

If the machine is down, glass beads have to be casted by hand. The Cons are the sweaty character of the work, the Pros the quick procedure, the fast cleaning of the thinner Pt crucibles, and the almost unlimited number of pills possible every day.

3.5.1 Preparations

The sample powders are to be prepared exactly the same way as in the procedure for the automated casting. The thinner crucibles are numbered.

3.5.2 Melting

Place the powders in Pt/Au (95/5) crucibles into the oven and melt them during about 30 minutes at 1150°C. $Li_2B_4O_7$ lowers the melting point to ca. 650-700°C, the melt is of low viscosity and can easily be homogenized by shaking. Sometimes, solid to viscous powder remnants stick to the inner walls. They have to be reunified with the melt. Tilt the crucible until the remnants are covered by melt and place it into the oven. Repeat this procedure until the inner walls are entirely free of remnants. If the melt still shows bubbles after 10 minutes, keep shaking the crucibles and leave them in the oven a little longer.

3.5.3 Preparation of the casting dish

The casting dish gets heated to red above the special Bunsen burner. Open gas and air only slightly, so that the flame stays small but pointy.

3.5.4 Casting

Remove the melt quickly from the oven and empty the crucible onto the casting dish.
Immediately put the crucible down, and adjust the casting dish to horizontal (note symmetric cooling patterns). Immediately switch off the gas (not the air) to let the melt quench.

3.5.5 The bead

Once the glass is quenched and detaches from the dish (clicking noise), empty the dish onto a towel. The measurement side is the side that faced the dish and must not be touching the towel while still hot.
Once you are sure the bead is not cracking, put the crucible back into the oven for 10 minutes and rapidly quench it in the Ultrasonicator in order to remove any melt remnants. Never scratch the crucible inside!! Put it into the acid bath for a few minutes to clean it.

3.5.6 Storage and transport of glass beads

There are one-way round plastic containers and foam inserts in the lab. They can be used for bead storage. Im Labor sind runde Plastikdosen und Schaumstoffeinlagen. For longer storage times, keep them in a dessicator. The $Li_2B_4O_7$ is strongly hygroscopic. For transport to EMPA, get a transport tray from the lab assistant.

4. Lab Rules

1. **The lab has to be kept tidy and has to be completely cleaned after use. Empty trash and close vent valves in the crushing room.**

2. **Report machine errors, missing or almost empty supplies, and broken parts to the lab assistant.**

3. **The lab key CO 25**

   The key and platinum tools are handed out to individuals who have signed up, are introduced to the protocols by the lab assistant or authorized substitute (personal uthorization by Prof.V. Dietrich), and accept the lab rules and the "Reglement" (see lab book). It is never to be taken outside the building (e.g. lunch, overnight). Signed-up users accept full responsibility for the lab (both rooms). Users are held individually legally responsible for anything broken, stolen, left dirty or damaged. These responsibilities partially expire after signing of the lab book (in E 18), and handing back of Platinum and lab key. The same rules apply for use of the crushing room only.

4. **Report missing supplies to the lab assistant.**

The followingviolations and non-observance of the lab rules may lead to payment of compensation to the IMP and to exclusion from any further lab work:

1. Scratching of crucibles and/or casting dish

2. Handing the lab key over to a third person without permission/note in the lab journal

3. Not reporting damages

4. Not reporting damages on the machine (Perl'X3):
- **Placing hot crucibles on polymer surfaces**
- **Changing pre-valve settings of cooling water and/or pressurized air**

5. Casting of glass beads from non-silikate materials:
- no metallic (esp. sulfidic) ores
- no sulphates
- no slags or cinders

If you plan to cast such materials, you must seek advice with the lab assistant first.

6. Casting of glass beads from more than 6 g total mass (powder + flux)

7. Not removing beads from the casting dish.