

## APPENDIX A6: SILLS: A MATLAB-BASED PROGRAM FOR THE REDUCTION OF LASER ABLATION ICP-MS DATA OF HOMOGENEOUS MATERIALS AND INCLUSIONS

Marcel Guillong<sup>1</sup>  
Dimitri L. Meier<sup>1</sup>  
Murray M. Allan<sup>2</sup>  
Christoph A. Heinrich<sup>1</sup>  
Bruce W.D. Yardley<sup>3</sup>

<sup>1</sup> Department of Earth Sciences, Swiss Federal Institute of Technology, ETH Zürich, Switzerland

<sup>2</sup> Anglo American Exploration (Canada) Ltd., Vancouver, BC, Canada

<sup>3</sup> School of Earth and Environment, University of Leeds, Leeds, U.K.

E-mail: guillong@erdw.ethz.ch

### INTRODUCTION

This paper describes a software package named SILLS (Signal Integration for Laboratory Laser Systems) designed for data reduction and concentration calculation of transient Laser Ablation ICP-MS signals, written in MATLAB (The MathWorks, Inc.). The software is primarily designed for user friendly and flexible data reduction to obtain quantitative analyses of fluid, melt or mineral inclusions enclosed in mineral or glass host, but can also be used for homogeneous samples. The transient nature of these signals demands a dedicated data reduction procedure, particularly if signals from inclusions and their chemically distinct host minerals need to be separated quantitatively from each other (Heinrich *et al.* 2003, Longerich *et al.* 1996).

The program includes a convenient and versatile option to display raw transient signals from the ICP-MS. Inclusion analysis, in particular, requires the visualization of each inclusion signal and the possibility to select integration intervals for gas blank, host mineral and inclusions precisely and flexibly. In contrast to other data reduction approaches, SILLS yields quantitative analyses of host and inclusion for a range of possible data reduction approaches without error-prone copy-paste steps between spreadsheets.

The software was first developed and used by M. Allan at Leeds University (Allan *et al.* 2005) and later intensively redesigned, extended and tested in a collaborative effort at the Institute of Isotope Geochemistry and Mineral Resources at ETH Zürich. The SILLS data import is tested to work with files from Agilent and Perkin Elmer ICP-MS directly and with Thermo Element 2 data after a MATLAB-based convert script, editable for

other instrument output files. The procedures and equations for concentration calculation are taken from the literature (Halter *et al.* 2002, Heinrich *et al.* 2003, Longerich *et al.* 1996) and are summarized in documents included with the software. All calculations are implemented according the most current knowledge, based on literature and in-house experience, but may still contain errors, thus requiring critical inspection of the results in every case. In particular, the calculation of uncertainties (Luo *et al.* 2007) on individual analyses and the calculation of limits of detection are undergoing continuous improvement, because no general applicable method has been published to date.

For further information about obtaining the software package and future updates, please visit <http://www.igmr.ethz.ch/research/fluids/software>.

### DESCRIPTION OF THE SOFTWARE

#### MATLAB and some general considerations

MATLAB is a flexible, relatively easy programming language that is well suited for graphical interfaces. The scripts are easy for people with a basic programming background to understand. All the data are stored and calculated using variables with different levels and sublevels in structures and matrices that can be accessed in MATLAB. Therefore there is no defined limitation in number of measured elements, number of time slices in a measurement or number of measurements in a project. The software was tested for up to 64 elements and 54 measurements. However, with increasing data volume, the calculations might become slower. A typical saved project file with 4 standards and 16 samples, measuring 50 elements

200 times per analysis is 2.5 Mb in size. A compiled standalone version is available for users without MATLAB.

It is possible to define parameters in no particular order. At any time, integration windows can be edited, a whole sample copied, the dwell times changed, and so on. The final results are calculated each time an output report is generated. At any time it is possible to save the project and continue working later.

### Main windows

SILLS consists of two main windows: The main control window and the calculation manager. When SILLS is started, the main control window (Fig. A6-1) appears. From this window, all data files are selected (load standards and load unknowns), projects are saved and opened, and basic settings can be set: input format (cps or counts), time format (described in the drift correction section), the standard reference material (SRM, load from file or create new), the dwell time and the flicker noise. When standards are loaded (described in next section), the SRM is assigned, as well as the time when the analysis was stored on the computer (analysis time). Standards can be selected, plotted and deleted, unknowns can also be copied. When all essential files are loaded, the calculation manager window (described later in this report) can be opened.

### Graphical user interface for signal integration

The graphic user interface for the definition of integration intervals is described using the analysis of a fluid inclusion as example. Every time a standard or sample is loaded from the main control window a figure (e.g., Fig. A6-2) with the plotted transient signal appears. In this plot, the intervals of interest (IOI) are selected by click and drag with the computer mouse. The background (gas blank), up to three intervals for a signal (linked together to 1 signal) as well as up to two intervals for a possible host correction can be set either by click and drag or typing the time in seconds from the beginning of the signal. Intervals are visible in different colors. The definition of the IOIs is not limited to the time a signal is loaded, at any time IOIs can be changed or removed, reopening the window either from the main control window or the calculation manager. For comparison of several samples, multiple windows can remain open. To make this IOI selection as easy as possible a zoom tool and a custom selection of the visible elements is

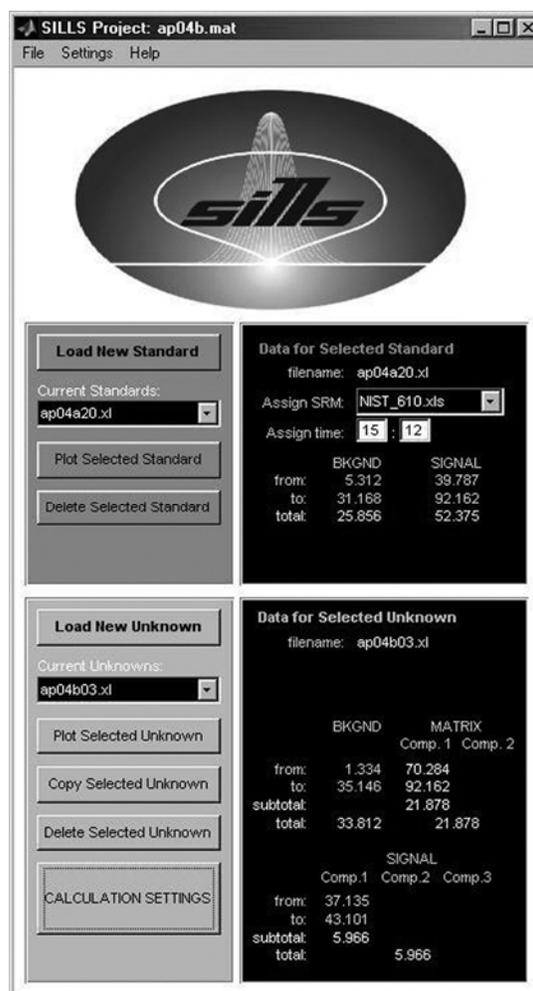


FIG. A6-1: The SILLS main window, used to handle project files, load measurements and standards and define basic settings.

implemented. By switching the display mode, background corrected count ratios (defined by the user) are plotted to help further to set the IOI. No matter which display mode is used and whatever elements are shown, the figures can be printed or saved as images in various raster or vector graphic formats. The spike/outlier detection can be accessed from the plots.

### Spike/outlier detection based on Grubbs test

An algorithm to identify and correct possible spikes or outliers has been implemented in the software. The whole dataset with intensities above a selectable threshold (e.g., 1000 cps) is tested for outlying points by the method described by Grubbs (Grubbs 1969). This test assumes a normal distribution, and compares the calculated statistic

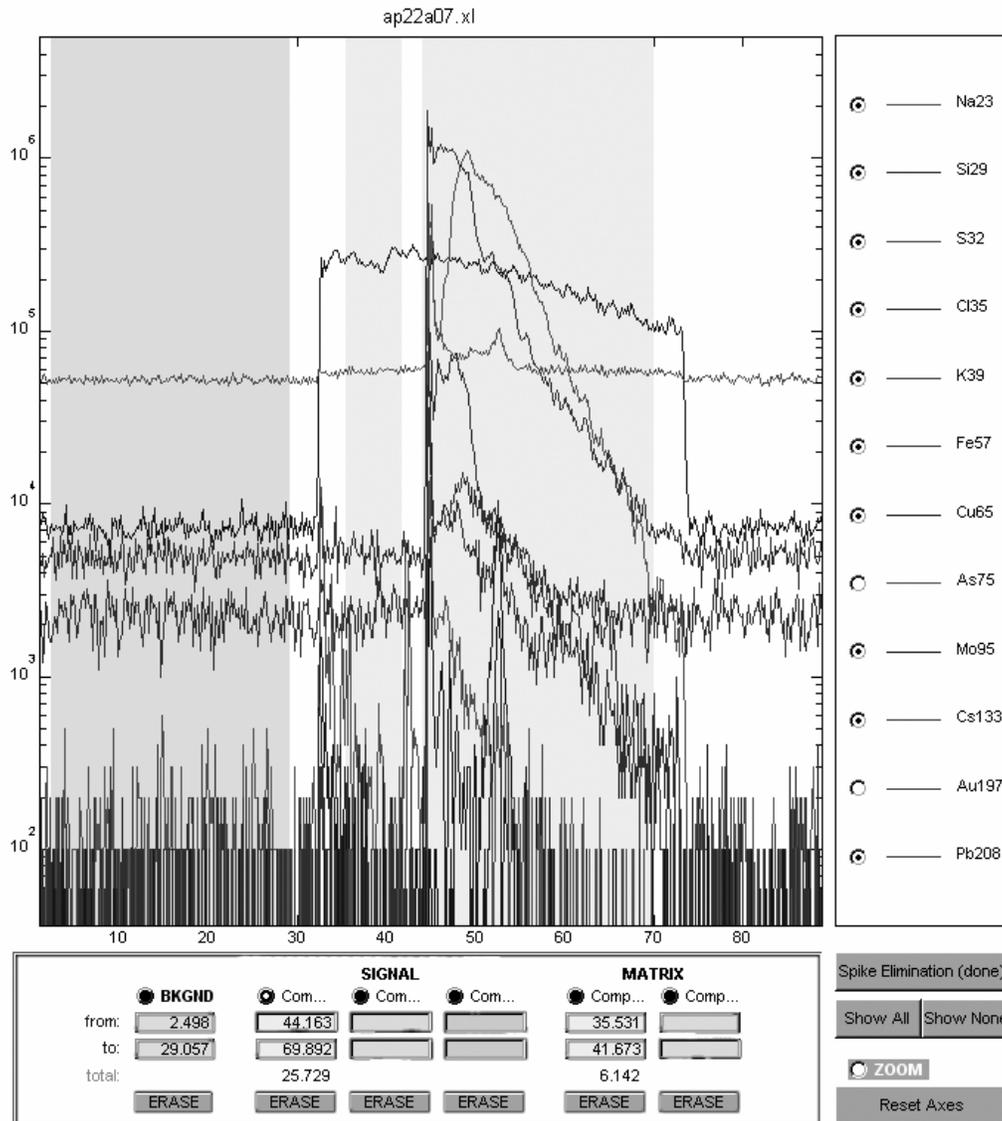


FIG. A6-2: Graphical user interface for definition of intervals of interest (IOI) in time-resolved signal intensity plots by click and drag, including a zoom function and spike elimination.

test value (STV, equation 1 below) with a tabled value depending on the number of measurements (7 in our case) and level of significance (1%, meaning the detected values are highly significant outliers):

$$STV = \frac{|x^* - \bar{x}|}{s} \quad (1)$$

where  $x^*$  is outlier suspected value,  $\bar{x}$  is mean, calculated with all values in the series, and  $s$  is standard deviation, calculated with all values in the series.

When outliers are detected, the software asks

the user to confirm the spike and to confirm that the outlier should be replaced with the calculated, suggested value (mean of the measurements before and after the detected spike), or another user defined value, or to keep the original value. Once a spike is corrected, the original values can only be recovered by reloading the original data file, which will remain unchanged as SILLS continues to be used.

Modification of outlier data is a controversial practice questioned by many scientists, including the authors. The Grubbs test algorithm provides an objective method for spike identification, and the

user has to confirm the modification for every single detected spike. This does not make the practice scientifically or methodologically valid. The rejection of outliers is more acceptable when it is done based on an underlying model or when the possible source of the spike is confidently known, *e.g.*, contaminant particles accidentally mobilized into the ICP-MS from the transport or ablation system.

### Drift correction and quality control

With SILLS, it is possible to correct for instrumental drift based on repeated analyses of standard reference material. So far only a linear drift correction based on changes in relative sensitivity is applied and visualized as shown in Figure A6-3. Times can be defined either using real clock analytical time or integer time points. It is possible to retrieve the analytical times from the file information. Using analytical times, the applied drift correction is closer to the real drift especially when there are breaks between the measurements of a run. For the visualization as shown in Figure A6-3, a drift correction standard that is assumed to have no drift can be chosen and the relative sensitivity of all measured elements can be plotted. The drift in relative sensitivity (compared to the drift correction standard) is plotted *vs.* the time for

individual elements or for all elements in percent. This overview gives the user control over the quality of the standard measurements. Problems with standard measurements become visible in this overview.

After instrument warm up, the observed drift by repeated standard reference material analysis may be found to be completely random, and not linear. In this case, to apply no drift correction, the time format parameter can be set to one integer time step (everything is assumed to be measured at the same time) and the mean relative sensitivities from the repeated SRM analysis without drift correction are used for quantification.

### Quantification possibilities / calculation manager

SILLS allows a set of quantification possibilities to fit most applications in LA-ICP-MS. The calculation manager window is shown in Figure A6-4. All unknown samples loaded show up in this window and they can be plotted, copied or deleted. A description can also be entered. In two rows, the parameter settings for the matrix (or host) and inclusion (or just the sample) are entered. Without a matrix (or host) correction for the inclusion, quantification is straightforward by selection of an internal standard concentration (either a known concentration of an element or a

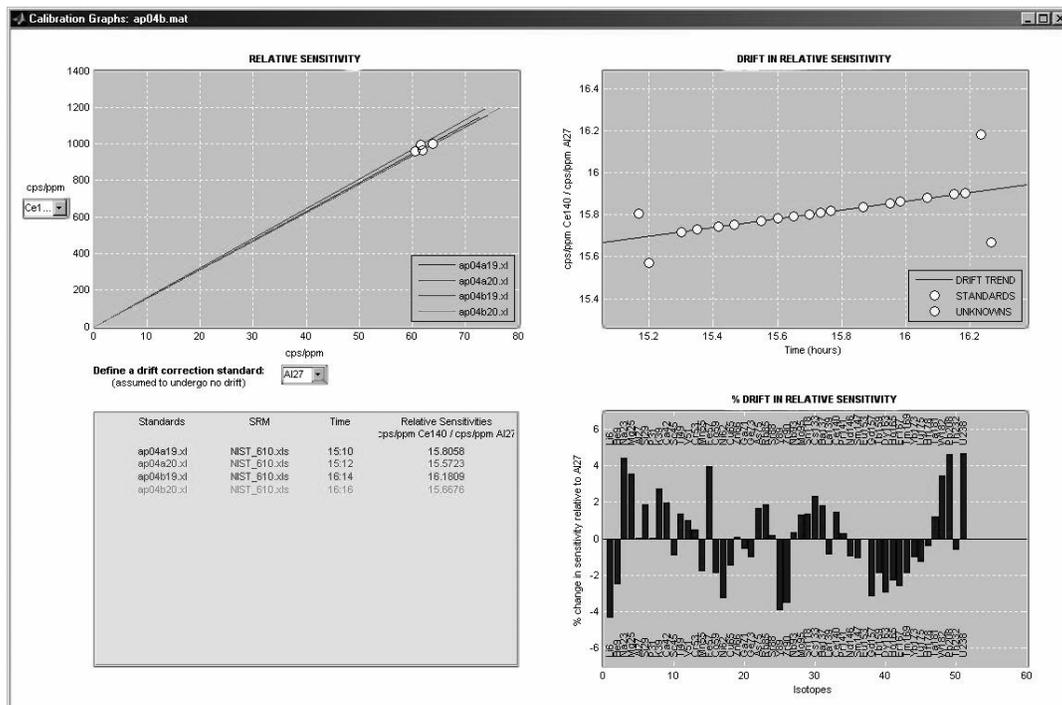


FIG. A6-3: Quality control window, including options for drift correction. See text for details.

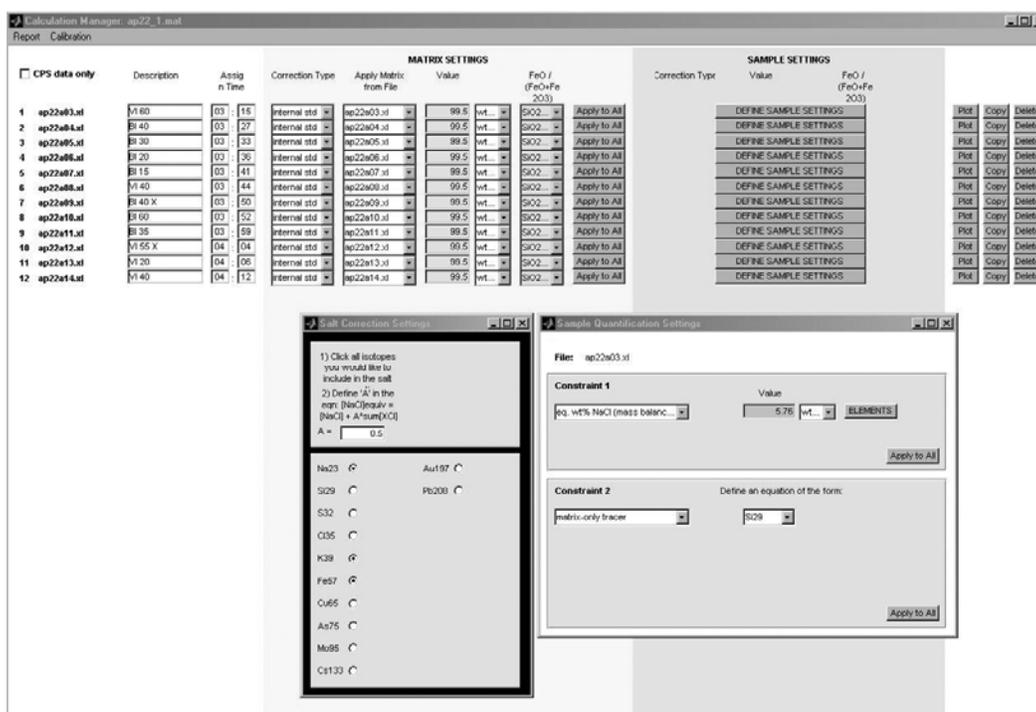


FIG. A6-4: Calculation manager window, including options for sample settings and the “salt correction” window.

calculation to the sum of all major oxides in wt.% (e.g., 96 wt.% when a water content of 4% is known) with a defined FeO/(FeO+Fe<sub>2</sub>O<sub>3</sub>) ratio). The calculation to 100 wt.% oxide (Guillong *et al.* 2005) requires the measurement of all main cations and can have systematic errors due to unknown amounts of water, anions other than oxygen and other restrictions and has to be used with care. For fluid inclusions, the user can define a NaCl equivalent concentration and select the cations that are implemented in the correction (the “salt correction”), either by charge balance or mass balance (Heinrich *et al.* 2003).

If a matrix (or host) correction is applied, two more constraints are necessary for quantification:

1. For the host, an internal standard is needed (again with an element of known concentration or 100 wt% oxide);
2. For the inclusion, the user must know two separate concentration constraints. A special case is the assumption that one element is only present in the host and not in the inclusion is referred to as a “matrix only tracer”. A second special case is often the assumption of 100 wt.% oxide instead of an individual element concentration. A third special case can be that not a single element concentration is known, but an equation (2) can be given:

$$\frac{X}{Y} = p \left( \frac{M}{N} \right)^2 + q \left( \frac{M}{N} \right) + r \quad (2)$$

where X, Y, M and N are measured elements and p, q and r are constants. These two constraints allow calculation of the fraction of a mixed signal that is attributable to the inclusion and, consequently, also the concentrations in the inclusion.

It is possible either to define the host in the same measurement as the inclusion or in a separate measurement. The equations for quantification are from the literature (Günther *et al.* 1998, Halter *et al.* 2002, Heinrich *et al.* 2003, Longerich *et al.* 1996) and are summarized in a document that comes with the software. If the user only needs to determine gas blank corrected intensities or ratios (e.g., isotope dating technique), without any concentration calculations, there is a box to check which allows all concentration calculations to be skipped.

### Report writing possibilities

The output can be formatted according to the different needs or preferences of measurement and application type. There are several preferences selectable for the output report. In the menu of the calculation manager the user can define whether the

major elements are shown as wt.% oxides or as  $\mu\text{g g}^{-1}$ . There is also the possibility to set the limit of detection (LOD) filter factor, which will show data that are below the LOD calculated as suggested in the literature (Günther *et al.* 1998, Halter *et al.* 2002, Heinrich *et al.* 2003, Longerich *et al.* 1996). As soon as the option “create output report” in the calculation manager is selected, a preview of the sample concentrations appears, to check whether the results are plausible. At this stage many parameters (*e.g.*, concentrations in host and inclusion, limits of detection, gas blank count rate, gas blank corrected count rate for host and inclusion, ratios including the error and the details to the individual analysis) can be selected to be included in the final output report. Once selected, the report is created and saved as an Excel spreadsheet.

#### SUMMARY AND AVAILABILITY

This software was specifically designed for inclusion analysis but can also be used for all other kind of applications (*e.g.*, homogeneous solids). It is intuitive and user friendly due to a graphical user interface, especially with respect to the choice of the integration of intervals of interest (IOI) by click and drag with the mouse. All necessary parameters can be controlled by the user.

A trial version and information about availability of the fully working version are given at: <http://www.igmr.ethz.ch/research/fluids/software>.

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