

Electronic Supplementary Information

A. Relative sensitivity coefficients (RSCs)

The Relative Sensitivity Coefficient (RSC) for an element in the sample is obtained by dividing measured elemental concentration, X_m by the expected concentration, X :

$$(1) RSC_X = \frac{X_m}{X}$$

For well-defined chemical compositions as it is typically the case for NIST standard research material (SRM), the atomic fractions are stated or have to be derived from the given mass fractions. The mass spectrometric measurements yield atomic intensities and their fractions are calculated by dividing atomic intensities of given element to all atomic intensities measured in the sample. By comparing the measured fraction of element X with the expected in the sample fraction one obtains RSC of the element. This can be summarised in Equation 2:

$$(2) RSC_X = \frac{A_X / A_{tot}}{P_X}$$

where A_X stands for the intensity determined for specie X , A_{tot} is the intensity determined for all elements stated in the sample or atoms in particular chemical formula. Hence, A_X/A_{tot} is the measured fraction of given element in the sample. P_X denotes the stated fraction of the element X in the sample (number of atoms X to all atoms in the sample).

Now we consider the data obtained by the linear correlation method. This method yields measurement of the concentration ratios between element X_{mi} and element Y_m , where m denotes the measured concentrations. Applying Equation 1 (definition of RSC coefficient), we obtain $X_{mi} = RSC_{Xi} \cdot X_i$ and $Y_m = RSC_Y \cdot Y$ where X_i and Y_i are expected concentrations of these elements, respectively. Combining these equations we derive formula for calculation of RSC coefficient of element X_i from the ratio of concentrations (or slope coefficient) of elements chosen in linear correlation:

$$(3) RSC_{Xi} = RSC_Y \frac{X_{mi} Y}{Y_m X_i}$$

Hence, knowing RSC_Y the ratio of measured concentrations X_{mi}/Y_m (slope coefficient in linear correlation of atomic intensities), the expected ratio of element Y to element X_i , one can derive RSC of contributing elements. The atomic intensities are obtained by integration of relevant isotope mass peaks and normalisation to full atomic abundance.

a) RSCs of C, O and Ca determined on pure calcium carbonate phase

We apply this definition to obtain RSCs of elements in a pure calcium carbonate phase. The elemental analysis conducted on the composite spectrum obtained by merging individual mass spectra yields atomic intensities expressed in #e- (number of collected by the detector electrons) (Table 1). From these data we calculate atomic fractions and compare to the atomic fractions expected in CaCO_3 :

Table 1: Determination of RSCs for the elements on a pure calcium carbonate phase with formula 2.

Element	Atomic intensity [#e-]	Error	Measured atomic fraction in CaCO_3	Expected atomic fraction in CaCO_3	RSC
C	1.830E10	1.77E8	0.11 ±02	0.2	0.55±0.03
O	3.670E10	3.94E8	0.22 ±0.01	0.6	0.36±0.04

Ca	11.181E10	1.91E8	0.67 ±0.03	0.2	3.30±0.05
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Now we apply this method to derive RSC of C and O in calcium carbonate mineral and compare the results obtained by using the first method (Equation 2). The RSC of Ca determined by the first method is taken now as a reference. The slope coefficients of C/Ca and O/Ca, the expected concentration ratios and the RSC of C and O determined with this method are shown in Table 2.

Table 2: Determination of RSCs of C and O on a pure calcium carbonate phase with formula 3. Note that RSC_{Ca} of 3.3 (Equation 2) is applied here as reference.

Element	X_i/Y_i : slope coefficient in linear correlation	Y/X expected from chemical formula	RSC of Ca determined from Eq. 2	RSC determined from Eq. 3 using $RSC_{Ca} = 3.3$
C	0.19±0.01	1	3.30±0.04	0.63 ±0.02
O	0.28±0.3	0.33	3.30±0.04	0.30 ±0.03

b) RSCs of C, O and Ca determined on the inclusion location

Linear intensity correlations C/Ca and O/Ca of the part of the data indicate presence of calcium carbonate in these locations. We chose the data from location 5 to repeat the calculations shown above to determine RSC of C, O and Ca at the inclusion. We determine first the RSCs by the analysis of composite spectrum. The results from this analysis are shown in Table 3.

Table 3: RSCs of C, O and Ca determined from composite spectrum on location 6

Element	Atomic intensity [#e-]	Error	Measured atomic fraction in $CaCO_3$	Expected atomic fraction in $CaCO_3$	RSC
C	1.755E11	4.32E8	0.18±0.03	0.2	0.91 ±0.05
O	2.731E11	3.94E8	0.28±0.02	0.6	0.44 ±0.05
Ca	5.267E11	1.91E8	0.54±0.03	0.2	2.71 ±0.04

Table 4: RSCs of C, O and Ca determined from linear correlations on location 5. Note that $RSC_{Ca} = 2.7$ taken from the Table 3 is applied here as reference.

Element	X_i/Y_i : slope coefficient in linear correlation	Y/X expected from chemical formula	RSC of Ca determined from Eq. 2	RSC determined from Eq. 3 using $RSC_{Ca} = 2.71$
C	0.36 ±0.02	1	2.71 ±0.04	0.97 ±0.09
O	0.43 ±0.03	0.33	2.71 ±0.04	0.38 ±0.05

We notice that the RSCs coefficients of C and O are larger, and RSC of Ca is smaller indicating improved stoichiometry of atomic ionisation at the location of the inclusion. The discrepancy of about 15% between the results obtained by these two methods is found.

c) RSCs of elements forming oxides and sulphides using formula 3 (see also Fig. 6)

a. Oxides

Table 5: RSCs of several elements determined by considering their oxides (hydroxides) present in inclusion. For each an element relevant chemical compound is indicated.

Element	X_i/Y : slope coefficient in linear correlation	Y/X expected from chemical formula	RSC of O	RSCs determined on various compounds	Average value of RSC element
Fe_{FeO}	3.30 ± 0.03	1	0.38 ± 0.05	1.25 ± 0.04	1.15 ± 0.05
$Fe_{Fe(OH)_2}$	1.41 ± 0.01	2	0.38 ± 0.05	1.06 ± 0.05	
Mg_{MgO}	1.91 ± 0.15	1	0.38 ± 0.05	0.72 ± 0.04	0.71 ± 0.05
$Mg_{Mg(OH)_2}$	0.91 ± 0.01	2	0.38 ± 0.05	0.70 ± 0.06	
$Si_{Si(OH)_2}$	0.74 ± 0.2	2	0.38 ± 0.05	0.56 ± 0.04	0.56 ± 0.04
$Al_{Al(OH)_3}$	0.72 ± 0.3	3	0.38 ± 0.05	0.82 ± 0.07	0.82 ± 0.07

b. Sulphides

We take into account RSC of Fe to calculate RSC of S. Two linear correlations are consistent with presence of FeS and $Fe(SH)_2$.

Table 6: RSC of S determined from RSC of Fe. Relevant chemical compound is indicated.

Element	X_i/Y : slope coefficient in linear correlation	Y/X expected from chemical formula	RSC of Fe	RSCs of S	Average RSC of S
S_{FeS}	0.47 ± 0.01	1	1.15 ± 0.05	0.54 ± 0.06	0.55 ± 0.04
$S_{Fe(SH)_2}$	0.99 ± 0.04	0.5	1.15 ± 0.05	0.57 ± 0.04	

Table 7. RSCs of elements derived from the analysis of sulphides present in the inclusion material by applying formula 3. RSC of S is taken as reference for the determination of RSCs of Ni, Co, Ti, Mg, Ca, and Al. For each an element relevant chemical compound is indicated.

Element X	X/S : slope coefficient in linear correlation	S/X expected from chemical formula	RSC of S	RSC of element X
Ni_{NiS}	0.40 ± 0.07	1	0.55 ± 0.04	0.22 ± 0.01
Co_{CoS}	0.34 ± 0.07	1	0.55 ± 0.04	0.19 ± 0.03
Ti_{TiS_2}	0.32 ± 0.01	2	0.55 ± 0.04	0.36 ± 0.05

$Mg_{Mg(SH)_2}$	0.66 ± 0.03	2	0.55 ± 0.04	0.68 ± 0.05
$Ca_{Ca(SH)_2}$	2.57 ± 0.04	2	0.55 ± 0.04	2.87 ± 0.05
$Al_{Al_2S_3}$	0.98 ± 0.02	1.5	0.55 ± 0.04	0.80 ± 0.05

The composite RSCs of the investigated elements are summarised in Table 8.

Table 8: Relative sensitivity coefficients (RSCs) determined from the intensity correlations (see Figs. 4 and 6). RSCs larger and smaller than 1 indicate larger and smaller than expected atom ionisation efficiencies, respectively. The relative statistical errors of the RSC determination are typically within a few per cent. The RSC coefficients determined on oxides and sulphides can have uncertainty of about 20 % (see text for the details).

Element	RSC	Element	RSC
C	0.97 ± 0.09	Ti	0.36 ± 0.05 Expected >1
O	0.38 ± 0.05	Fe	1.15 ± 0.05
Ca	2.71 ± 0.04	Mg	0.71 ± 0.05
Si	0.56 ± 0.04	Ni	0.22 ± 0.01 1 expected
S	0.55 ± 0.04	Co	0.19 ± 0.03 1 expected
Al	0.82 ± 0.07	Na, K	>1 expected

B. Elemental detection limits

The atomic (elemental) concentrations are derived from the mass spectrometric analysis on location 8 and the elemental concentrations are corrected with RSCs of major and minor elements Table 1. The dynamic range of the mass spectra is observed to be larger than 10^4 . The measured atomic concentrations are shown in Fig.1_ESI. The background values are at the level of 10^7 . Table 2 relative atomic fractions are plotted in Fig. 2_ESI.

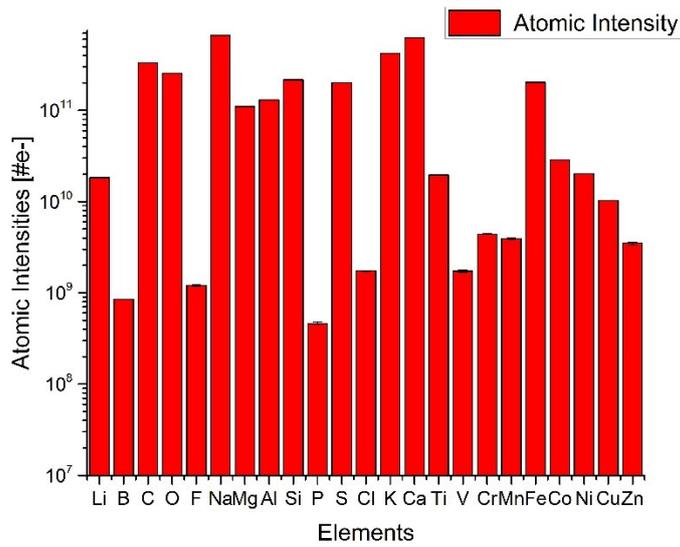


Fig.1_ESI. Atomic intensities of all elements determined from the mass spectra measured at location 8.

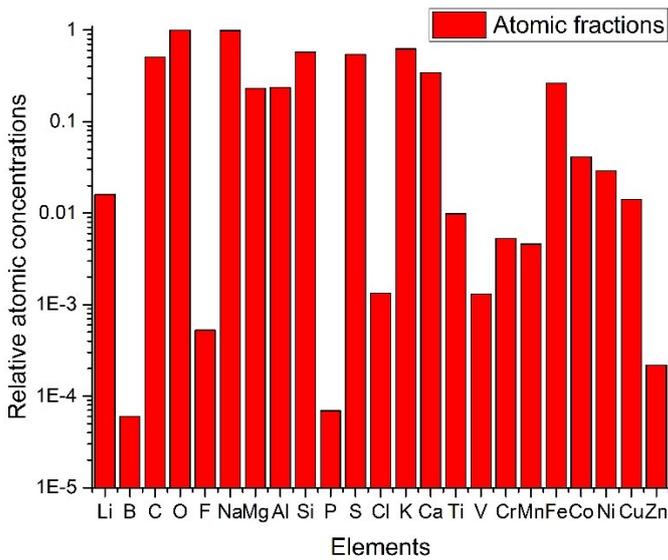


Fig. 2_ESI. The atomic fractions of the elements measured on Location 8. All atomic concentrations are added and are normalized to one. The atomic fractions of the F, P and Cl elements are expected to be lower than plotted (here, we assume their ionisation efficiency to be 1 but they expected to be lower than for Si or S).