**Supplementary document for estimation of K content in mineral inclusions and crystal lattice of quartz grains.**

This document gives an overview of the basic calculations we performed to get an estimate of the amount of K in mineral inclusions in quartz and/or from the K in the quartz crystal lattice. Note, that the calculations are only intended to get an idea of the order of magnitude of the K-content to assess if and how this can affect our age calculation and interpretations. The results reported are therefore not very precise.

**K (and 40Ar) from Mineral Inclusions**

Consecutive steps to calculate K content:

1. We dated cleaned quartz with a grainsize of 400-500 μm. We assume that these quartz grains are either cubic or spheric. With this information we can estimate the surface (S), volume (V) and mass (M) of 1 quartz grain for four scenarios (400 μm cubic, 400 μm spheric, 500 μm cubic, 500 μm spheric):

**Cubic:**

**S = a2** “a” is grain diameter and is either 400 μm or 500μm, unit of S is **μm2**

**V = a3** “a” is grain diameter and is either 400 μm or 500μm, unit of V is **μm3**

**M = V × ρ** ρ is density: we used 2.63 g/cm3 = 2.63×10-12 g/µm3 = 2.63×10-12×106 µg/µm3 = 2.63×10-6 µg/µm3. Unit of M is µg.

|  |  |  |
| --- | --- | --- |
| Cubic | 400 µm | 500 µm |
| S | 0,16×106 µm2 | 0,25×106 µm2 |
| V | 64×106 µm3 | 125×106 µm3 |
| M | 168 µg | 329 µg |

**Spheric:**

**S = π × R2** R is radius (0.5×diameter) of either 400μm or 500μm, unit of S is **μm2**

**V = 4/3 × π × R3** Unit of V is **μm3**

**M = V × ρ** ρ is density: we used 2.63×10-6 µg/µm3. Unit of M is µg.

|  |  |  |
| --- | --- | --- |
| Spheric | 400 µm | 500 µm |
| S | 0,13×106 µm2 | 0,20×106 µm2 |
| V | 33×106 µm3 | 65×106 µm3 |
| M | 88 µg | 172 µg |

1. For each experiment we reported the mass of the analyzed samples. From this information we can derive the number of grains we approximately analyzed:

**Number of Quartz Grains used for analysis**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | Weight (mg) | Cubic 400µm | Cubic 500µm | Spheric 400µm | Spheric 500µm | Average\* |
| R1a BNV | 46 | 274 | 140 | 523 | 267 | 301 |
| R1b BNV | 25 | 149 | 76 | 284 | 145 | 164 |
| R2 BPV | 30 | 179 | 91 | 341 | 174 | 196 |
| R2.1 BNV | 22 | 131 | 67 | 250 | 128 | 144 |
| R3 BPV | 30 | 179 | 91 | 341 | 174 | 196 |
| R4 BPV | 31 | 185 | 94 | 352 | 180 | 203 |
| R5 BNV | 32 | 190 | 97 | 364 | 186 | 209 |
| R6 BPV | 35 | 208 | 106 | 398 | 203 | 229 |

\*Average of 4 options is used as estimate for number of grains per sample

1. We estimate the average MI surface (μm2) and multiply this with the number of MI as observed/counted in one intersection in one grain:

**Estimated Surface 1 MI (μm2) × number of MIs observed in 1 quartz grain = Total Surface MI (μm2) for 1 intersection in 1 quartz grain**

1. We then approach the percentage of MIs in 1 quartz grain by dividing the **Total Surface MI (μm2) for 1 intersection in 1 quartz grain** with **the surface of the intersection (S in step 1)**:
2. We can transfer this percentage into a volume estimate of MIs in 1 quartz grain:

**% MI in Quartz / 100 × V1 qtz grain= VMI in 1 qtz grain (µm3)**

See step 1 for V1 qtz grain (in µm3)

1. We assume also a density of 2.63 g/cm3 = 2.63×10-6 µg/µm3 for the MIs and use this to convert MI volume to MI mass in 1 quartz grain:

**VMI in 1 qtz grain (µm3) × 2.63×10-6 µg/µm3 = MMI in 1 quartz grain (µg)**

This can then be multiplied by the number grains in a sample (step 2), to arrive at the total mass of MI analyzed in an experiment.

**MMI in 1 quartz grain (µg) × numbers of grains analyzed = MMI in sample (µg)**

1. We obtained K content for both quartz crystal lattice and mineral inclusions from EMPA data. EMPA reports in wt% K. We convert wt% K to ppm by multiplying with 104.

**wt% K × 104 = ppm K**

1. To estimate amount of K derived from MI in a sample:

**Amount of K (μg) = MMI in sample (μg) × K (ppm) × 10-6**

The amount of K in µg can be converted to mol by dividing it by the molar mass of K (39.10 g/mol = 39.10 × 106 µg/mol)

**Amount of K (μg) / (39.10 × 106 µg/mol) = Amount of K (mol)**

The amount of 40K (0.012% of total K) in a sample is then derived from

**40K (mol) = K (mol) × 0.012 / 100 from mineral inclusions per sample.**

1. The amount of radiogenic 40Ar (40Ar\*) that can originate from the K stored in MIs depend on the age of the MIs.

Rewritten into:

t is age in years, λ = 5.543×10-10 yr-1, λe = 0.581×10-10 yr-1, 40K is 40K form MIs in a sample (in mol), and 40Ar\* is amount of 40Ar\* that can originate from MIs in a sample (in mol).

1. The sensitivity of the Helix is 3.5×10-16 mol/fA. Therefore, the amount of 40Ar\* released from MIs in a sample can be calculated from 40Ar\* (mol) / (3.5×10-16 (mol/fA) = 40Ar\* (in fA).

This number can be compared to the amounts of 40Ar\* that we measured.

**K (and 40Ar) from quartz crystal lattice**

K content in the crystal lattice of quartz is below EMPA detection limits (<100ppm). We therefore use 100ppm K in quartz crystal lattice as maximum amount of K.

To estimate amount of K derived from quartz lattice in a sample:

**Amount of K (μg) = Msample (μg) × K (ppm) × 10-6**

The amount of K in µg can be converted to mol by dividing it by the molar mass of K (39.10 g/mol = 39.10 × 106 µg/mol)

**Amount of K (μg) / (39.10 × 106 µg/mol) = Amount of K (mol)**

The maximum amount of 40K (0.012% of total K) in a sample is then derived from

**40K (mol) = K (mol) × 0.012 / 100 from quartz lattice.**

You then follow step 9 and 10 as described above.