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Supporting information for

**[The role of CO2 in the genesis of Dabie-type porphyry molybdenum deposits]**

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Supplemental material: Detailed descriptions of the experimental and analytical methods, additional results, modeling and the tectonic setting of Dabie-type Mo deposits.

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**Introduction**

[The supporting information (Text S1 to S4) presents additional results, including the concentrations of molybdenum in quenched glasses and equilibrium fluids, as well as complementary discussion of the main text. This supporting information provides data tables for the starting materials of this study (Supplementary Tables 1-2), microthermometric data (Supplementary Table 3), major and trace compositions of quenched glass (Supplementary Table 4), a summary of partitioning coefficient data (Supplementary Table 5), and molding results (Supplementary Table 6), respectively. The supporting information also includes the following figures: the diagram of the experimental set-up (Supplementary Figure 1); comparative results from two measurements (Supplementary Figure 2); LA-ICP-MS signals of brine fluid inclusions (Supplementary Figure 3); and variations in molybdenum concentration in quenched glass and fluid (Supplementary Figure 4)]

**S1. Additional results**

**1.1 The concentration of Mo in equilibrium fluids and quenched felsic glasses.**

As mentioned in the method section, fluid-melt partitioning experiments were conducted in the systems H2O-CO2, H2O-NaCl and H2O-NaCl-CO2 at 850 ℃ and 100 or 200 MPa. In the system H2O-CO2, *X*CO2 was varied between 0.10 and 0.20 and in experiments in the system H2O-NaCl, the proportion of NaCl was varied between 1.1 wt.% and 44 wt.%. The value of *X*CO2 and the proportion of NaCl in the system H2O-NaCl-CO2 varied from 0.11 to 0.31 and 2.2 to 3.1 wt.% in the brine and vapor, respectively, and in the brine, the proportion of NaCl was between 56 and 62 wt.%. The experiments all had a duration of 10-12 days. To establish whether this was sufficient to reach equilibrium, i.e., for any gradients in Mo concentration in the melt to be eliminated, the concentration of Mo and the major elements was analyzed along traverses from one edge of pieces of the quenched glasses to the other edge (Supplementary Table 4). The results show that there was no gradient in element concentration, that the relative standard deviation for the concentration of Mo was less than 20% and that, in the case of the major elements, it was less than 10%. This relatively homogeneous distribution of the elements in the glass shows that equilibrium was reached during the experiments.

The major element composition of the quenched glasses was generally very similar to that of the starting material. In experiments involving H2O-NaCl and H2O-NaCl-CO2 fluids, however, the concentration of K2O in the glasses displayed a small but progressive decrease with increasing salinity and CO2 content. This decrease was ≤1 wt.%, except in experiment KD-003, in which the fluid had an initial salinity of 42.6 wt.%; the K2O content of the quenched glass in this experiment decreased from 5.95 to 1.36 wt.%. Despite this decrease in K2O content, the A/NK (mole ratio of Al2O3 and Na2O+K2O of the quenched glasses) value of the melt in experiments involving H2O-CO2 and H2O-NaCl fluids remained unchanged. However, the A/NK ratio of the melt in experiments involving H2O-NaCl-CO2 fluids decreased slightly compared to that of the starting material due to a decrease in the Al2O3 content of the quenched glass.

The glasses from experiments with fluids in the H2O-CO2 system all had very similar Mo contents of ~ 400 ppm, despite the variation in *X*CO2. However, the concentration of Mo in the quenched glasses from the experiments with fluids in the H2O-NaCl system decreased with increasing fluid salinity, and in the experiments involving H2O-NaCl-CO2 fluids, it decreased with both increasing salinity and increasing CO2 content. The concentration of Mo in the quenched glass varied from 359 to 13.6 and 189 to 112 ppm, respectively, for the two fluid systems (Supplementary Figure. 4; Supplementary Table 5).

The Mo concentration of the reacted fluids in the H2O-CO2 system varied little and unsystematically with respect to *X*CO2. It ranged from 82 ppm to 117 ppm for *X*CO2 values between 0.1 and 0.2.

In the H2O-NaCl system, the concentration of Mo in this fluid increased with increasing salinity of the fluid from ~180 ppm for a salinity of 1.1 wt.% NaCl to ~430 ppm for a salinity of 21 wt.% NaCl. The concentrations of Mo obtained by the leaching and fluid inclusion methods (Supplementary materials 1.3) were indistinguishable within the experimental and analytical uncertainty of the two methods (Supplementary Figure 2a).

Brine and vapor were trapped as separate phases in the H2O-NaCl-CO2 system, as shown by the presence of vapor and brine inclusions, as well as heterogeneously (variable proportions of vapor and brine), in quartz from the experiments for this system (Fig. 1). To ensure that inclusions containing heterogeneously entrapped liquid and vapor were not considered in our evaluation of the composition of the vapor and brine inclusions and in determining *D*Mo, we only measured the compositions of fluid inclusions in fluid inclusion assemblages for which the phase ratios were consistent1. As a result of the phase separation, the salinity of the brine increased from that of the homogeneous system (~7 wt.%) to 56 wt.% NaCl at a *X*CO2 of 0.1 and 62 wt.% NaCl at a *X*CO2 of 0.3. The corresponding maximum concentrations of Mo in the brine were 11,452 ppm and ~20,000 ppm (KD-005 and Q-017). Because of the large bubble size of the vapor inclusions (>80% of the inclusion volume) (Fig. 1c), there was a large variation in the clathrate melting temperature and a correspondingly large uncertainty in the estimated salinity of the vapor inclusions (Supplementary Table 3). The average salinity of these inclusions was ~ 3.1 wt.% NaCl for a *X*CO2 of ~0.1 and 2.2 wt.% NaCl for a *X*CO2 of 0.31 and the concentration of Mo was ~ 400 ppm.

**1.2 The fluid-melt partition coefficient for Mo (*D*Mofluid/melt** **)**

The data for *D*Mofluid/melt obtained in this study are summarized in Supplementary Table 5 and the specific results are reported in the results section of this paper.

**1.3 The influence of salinity on *D*Mo**

Although the *D*Mofluid/melt values increase with increasing salinity in the lower salinity part (≤ 20 wt.%) of the H2O-NaCl system, this increase is relatively small (0.7 to 3.2). In contrast, in the high salinity part (≥ 20 wt.%) of the H2O-NaCl system, the increase in the *D*Mofluid/melt value is large, reaching 25.7 at a salinity of 44.3 wt.% NaCl, i.e., the variation of *D*Mofluid/melt with salinity is exponential. Thus, hypersaline fluids are very efficient in leaching Mo from coexisting felsic melts. Indeed, in the brine-vapor-melt system, the *D*Mobrine/melt value reached 179 at a salinity of 62 wt.% NaCl (*X*CO2 = 0.3). Thus, based on the Mo concentration of the melt employed in our experiments, the solubility of Mo in such a brine could reach ~ 20,000 ppm. We are not implying, however, that such a high concentration might be realized in nature as the Mo concentrations of the magmas are likely to be much lower than those of the melt employed in our experiments.

**S2. Comparison of *D*Mo values to published values**

Because the value of *D*Mofluid/melt is a function of a number of parameters, notably pressure, temperature, *f*O2, *f*S2, and the melt and fluid composition2–8, it is difficult to reliably compare the values of *D*Mofluid/melt obtained in the different studies, including ours. Several studies, however, have reported trends of *D*Mofluid/melt with salinity similar to that reported here4–7. In all cases the *D*Mofluid/melt value for the high salinity fluids was reported to be ≥ 100 times higher than that for the low salinity fluids (Fig.3). The values reported by Tattitch and Blundy5, and Fang and Audetat6 are consistently higher than those of the current study. A possible reason for this is the presence of sulfur in their experiments, which is interpreted by the the authors of these papers to increase the solubility of Mo in the fluids relative to that of Mo in sulfur-free experiments (Fig.3).

**S3. Modeling the efficiency of molybdenum extraction from magmatic fluids**

The efficiency of molybdenum extraction from magmatic fluids is defined as the amount of Mo in the fluid exsolved from the magma divided by the amount of molybdenum initially in the magma. In calculating this efficiency of extraction, a hypothetical chamber containing 100 km3 of magma with a concentration of 15 ppm Mo9, a water content of 5 wt.%, and a density of 2.5 g/cm3 was assumed. The molybdenum in the hydrothermal fluid was assumed to have a 100% precipitation efficiency and the mass proportion of fluid exsolved from the magma was assumed to be 10%. Because the fluids in the H2O-NaCl-CO2 system were in the two-phase region under the experimental conditions, the brine and the vapor could be considered to represent the exsolution of fluid from a magma with the same composition as the melt. Based on the initial salinity of the H2O-NaCl-CO2 fluid, microthermometric estimates of brine and vapor salinity and the lever rule, the mass ratio of brine and vapor was determined to have been between 0.07 and 0.1. A mass ratio of 0.1 was used in the calculation of extraction efficiency. Accordingly, the bulk partition coefficient (*D*Mobulk = *D*Mobrine \* 1/11 + *D*Movapor \* 10/11) was recalculated in the H2O-NaCl-CO2 system based on this assumption (details of the calculation are provided in Supplementary Table 6). As the experiments for the H2O-NaCl-CO2 fluid-melt system employed a peralkaline rather than a peraluminous composition and *D*Mo values for the latter melt composition are approximately half those for peralkaline melts, the *D*Mo values were assumed to be half those measured. The H2O-NaCl fluid, however, was in the supercritical region under the experimental conditions and the *D*Mofluid/melt values could be determined directly from the measured concentrations of Mo in the fluid and the glass. In order to evaluate the role of CO2 in improving the efficiency of extracting Mo from magma, the *D*Mobrine/melt value for the H2O-NaCl-CO2 system was determined for a similar bulk salinity to that of the supercritical fluid in the H2O-NaCl system. The starting salinity of the H2O-NaCl-CO2 system is ~ 7 wt.%, and the *D*Mo obtained for a salinity of 6.3 wt.% of H2O-NaCl system was, therefore, used for calculation. The equation of was used to calculate the mass of Mo in the residual magma, where F represents the fraction of the exsolved fluids and D represents the partition coefficient. The extraction efficiency was defined as the mass of Mo extracted by the exsolved fluids divided by the mass of Mo in the initial magma.

**S4. The nature of the tectonism and magmatism associated with Dabie-type Mo deposits**

The Dabie-type porphyry molybdenum deposits developed in a post-collisional extensional environment. The tectonic change from collisional compression to extension was associated with collapse, delamination, and thinning of over-thickened orogenic crust and lithosphere, accommodating large-scale magmatism and mineralization10,11. As a result, the granitic rocks related to ore-formation are metaluminous to peraluminous, and high-K calc-alkaline to shoshonitic. In addition, the Sr/Y ratios of these crust-derived granites decrease with their age from ~140 Ma to <127 Ma, reflecting thinning from over-thickened crust to crust of normal thickness (<35 km) in the area10–12. The carbon isotope compositions of the fluid inclusions are in the range from -2.3 ‰ to +2.7 ‰13 suggesting that the CO2 of the magmas originated from a mixture of recycled carbonate rocks and mantle. Rare Au/Cu mineralization is associated with the Mo mineralization.

Supplementary Table 1. The initial composition of the glasses used in the experiments.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| T ℃ | P MPa | Na2O, wt.% | Al2O3,wt.% | SiO2, wt.% | K2O, wt.% | A/NK | Mo, ppm |
| CO2-H2O series | | | | | | | |
| 850 | 100 | 5.28 | 11.1 | 77.1 | 6.41 | 0.71 | 592 |
| NaCl-H2O series | | | | | | | |
| 850 | 200 | 3.92 | 12.4 | 77.6 | 5.95 | 0.96 | 656 |
| NaCl-CO2-H2O series | | | | | | | |
| 850 | 200 | 5.28 | 11.1 | 77.1 | 6.41 | 0.71 | 592 |

Supplementary Table 2. Initial fluid composition.

|  |  |  |
| --- | --- | --- |
| No. | Salinity, wt.% | *X*CO2, mol% |
| CO2-H2O-series |  |  |
| C-002 | N.D. | 0.1 |
| C-003 | N.D. | 0.15 |
| C-005 | N.D. | 0.15 |
| C-006 | N.D. | 0.2 |
| NaCl-H2O series |  |  |
| Q-004 | 4.93 | N.D. |
| Q-008 | 9.92 | N.D. |
| Q-001 | 6.94 | N.D. |
| Q-006 | 1.97 | N.D. |
| H-002 | 6.94 | N.D. |
| KD-001 | 14.8 | N.D. |
| KD-002 | 19.8 | N.D. |
| KD-003 | 42.6 | N.D. |
| NaCl-CO2-H2O series\* |  |  |
| Q-011 | 7.4 | 0.11 |
| Q-014 | 7.8 | 0.15 |
| Q-016 | 7.3 | 0.21 |
| Q-017 | 7.1 | 0.31 |
| KD-005 | 7.4 | 0.30 |

Note:

N.D. = no data.

\*As the decomposition of oxalic acid produces water, solid NaCl was added to ensure that the salinity of the starting solution in the NaCl-CO2-H2O series experiments corresponded to that selected.

Supplementary Table 3. Microthermometric measurements.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | *X*CO2 | Decomposition temperature of clathrate, ℃ | | Salinity of the vapor, wt.% | Dissolution temperature of halite, ℃ | Salinity of the brine, wt.% | Melting temperature of ice, ℃ | Salinity of the supercritical fluid, wt.% |
| Q-011 | 0.11 | 8.5-8.9 | 3.0-2.2 | | 472 | 56 | N.D. | N.D. |
| Q-014 | 0.15 | N.A. | N.A. | | 490 | 58 | N.D. | N.D. |
| Q-016 | 0.21 | 8.2-8.6 | 3.5-2.8 | | 494 | 59 | N.D. | N.D. |
| Q-017 | 0.31 | N.A. | N.A. | | 517 | 62 | N.D. | N.D. |
| KD-005 | 0.30 | 8.7-9 | 2.6-1.8 | | 515 | 62 | N.D. | N.D. |
| KD-001 | N.D. | N.D. | N.D. | | N.D. | N.D. | -12.7 | 17 |
| KD-002 | N.D. | N.D. | N.D. | | N.D. | N.D. | -18.3 | 21 |
| KD-003 | N.D. | N.D. | N.D. | | 370 | N.D. | N.D. | 44 |
| Q-006 | N.D. | N.D. | N.D. | | N.D. | N.D. | -0.6 | 1.1 |
| Q-004 | N.D. | N.D. | N.D. | | N.D. | N.D. | -2.3 | 3.9 |
| Q-001 | N.D. | N.D. | N.D. | | N.D. | N.D. | -3.9 | 6.3 |
| Q-008 | N.D. | N.D. | N.D. | | N.D. | N.D. | -7.2 | 11 |
| H-002 | N.D. | N.D. | N.D. | | N.D. | N.D. | -4.1 | 6.6 |

Note:

N.D.- no data.

N.A.- the data are not applicable because of the large uncertainty.

Supplementary Table 4 Major element composition of the quenched glass in wt%, and Mo concentration in ppm.

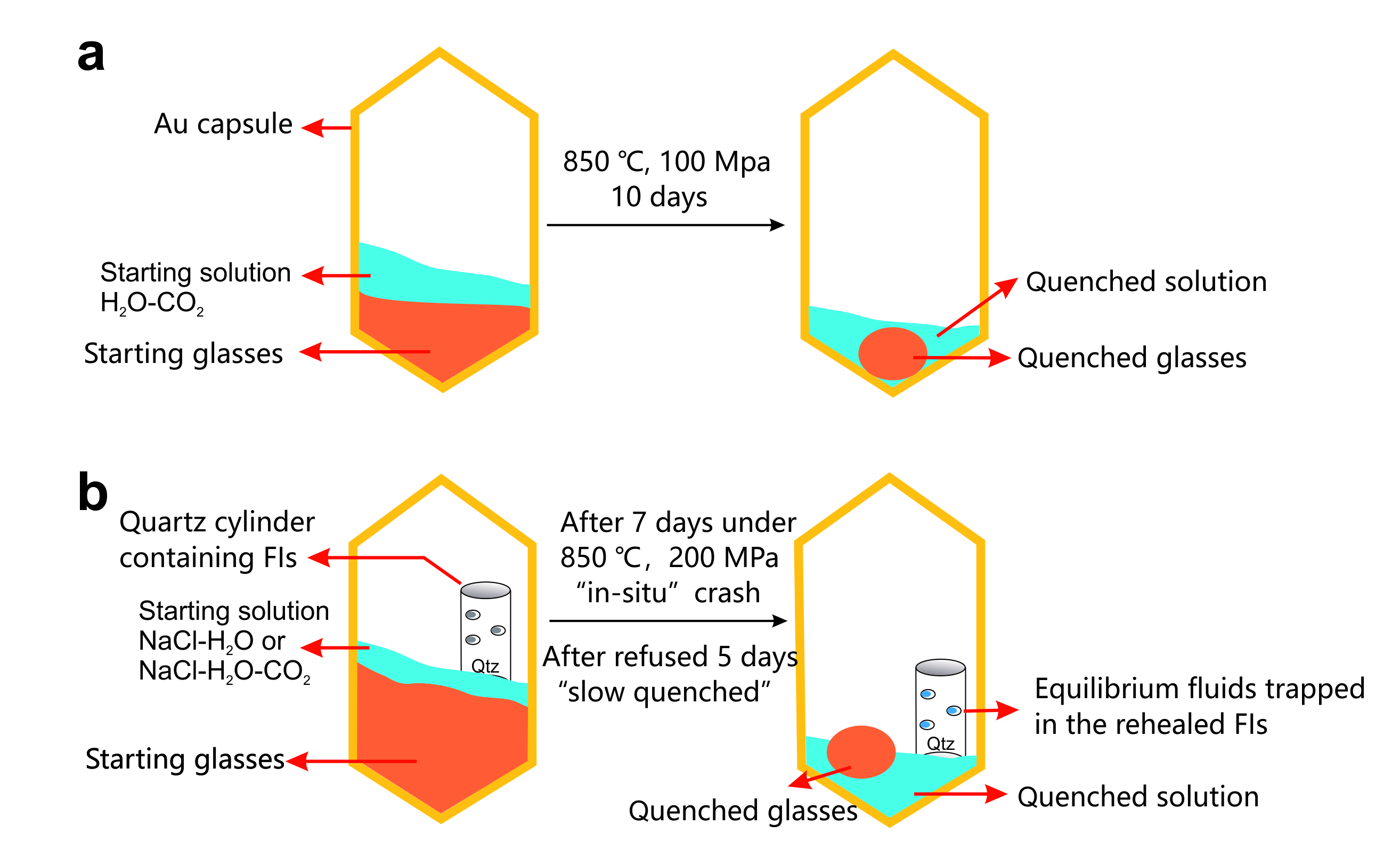
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | N | Na2O | σ | RSD | Al2O3 | σ | RSD | SiO2 | σ | RSD | K2O | σ | RSD | A/NK | Mo | σ | RSD |
| H2O-CO2 experiments | | | | | | | | | | | | | | | | | |
| C-002 | 6 | 5.14 | 0.04 | 0.78 | 10.9 | 0.19 | 1.74 | 77.5 | 0.23 | 0.30 | 6.42 | 0.02 | 0.31 | 0.71 | 401 | 2.06 | 0.51 |
| C-003 | 8 | 5.13 | 0.02 | 0.39 | 10.8 | 0.06 | 0.56 | 77.6 | 0.04 | 0.05 | 6.44 | 0.01 | 0.16 | 0.7 | 474 | 4.13 | 0.87 |
| C-005 | 8 | 5.13 | 0.06 | 1.17 | 10.8 | 0.21 | 1.94 | 77.6 | 0.32 | 0.41 | 6.48 | 0.06 | 0.93 | 0.7 | 456 | 6.68 | 1.46 |
| C-006 | 8 | 4.82 | 0.09 | 1.87 | 10.4 | 0.33 | 3.17 | 78.6 | 0.47 | 0.60 | 6.18 | 0.08 | 1.29 | 0.71 | 424 | 3.88 | 0.92 |
| NaCl-H2O experiments | | | | | | | | | | | | | | | | | |
| Q-004 | 8 | 3.53 | 0.22 | 6.23 | 11.7 | 0.62 | 5.30 | 78.8 | 0.93 | 1.18 | 5.94 | 0.58 | 9.76 | 0.95 | 277 | 14.9 | 5.38 |
| Q-008 | 7 | 4.46 | 0.16 | 3.59 | 11.2 | 0.54 | 4.82 | 79.9 | 0.79 | 0.99 | 4.48 | 0.1 | 2.23 | 0.92 | 162 | 28.4 | 17.5 |
| Q-001 | 8 | 4.7 | 0.13 | 2.77 | 11.2 | 0.27 | 2.41 | 79.8 | 0.47 | 0.59 | 4.3 | 0.47 | 10.9 | 0.9 | 228 | 18.3 | 8.03 |
| Q-006 | 7 | 5.09 | 0.34 | 6.68 | 12.9 | 0.74 | 5.74 | 78.0 | 1.34 | 1.72 | 3.97 | 0.15 | 3.78 | 1.02 | 359 | 83.4 | 23.2 |
| H-002 | 7 | 4.81 | 0.07 | 1.46 | 11.6 | 0.21 | 1.81 | 79.3 | 0.29 | 0.37 | 4.3 | 0.04 | 0.93 | 0.93 | 205 | 35.9 | 17.5 |
| KD-001 | 10 | 5.53 | 0.07 | 1.27 | 11.7 | 0.28 | 2.39 | 79.6 | 0.35 | 0.44 | 3.17 | 0.09 | 2.84 | 0.93 | 145 | 23 | 15.9 |
| KD-002 | 10 | 5.64 | 0.27 | 4.79 | 11.3 | 0.51 | 4.51 | 80.3 | 0.84 | 1.05 | 2.74 | 0.08 | 2.92 | 0.92 | 81 | 15.3 | 18.9 |
| KD-003 | 10 | 5.6 | 0.1 | 1.79 | 10.3 | 0.2 | 1.94 | 82.7 | 0.25 | 0.30 | 1.36 | 0.03 | 2.21 | 0.96 | 14 | 2.57 | 18.4 |
| NaCl-H2O-CO2 experiments | | | | | | | | | | | | | | | | | |
| Q-011 | 8 | 5.31 | 0.06 | 1.13 | 9.34 | 0.09 | 0.96 | 80.7 | 0.17 | 0.21 | 4.63 | 0.09 | 1.94 | 0.68 | 189 | 1.49 | 0.79 |
| Q-014 | 8 | 4.98 | 0.04 | 0.80 | 9.62 | 0.14 | 1.46 | 79.8 | 0.13 | 0.16 | 5.64 | 0.04 | 0.71 | 0.67 | 171 | 3.72 | 2.18 |
| Q-016 | 7 | 4.93 | 0.07 | 1.42 | 9.64 | 0.11 | 1.14 | 80.1 | 0.25 | 0.31 | 5.3 | 0.11 | 2.08 | 0.69 | 145 | 3.92 | 2.70 |
| Q-017 | 8 | 4.9 | 0.05 | 1.02 | 9.6 | 0.17 | 1.77 | 80.0 | 0.19 | 0.24 | 5.53 | 0.04 | 0.72 | 0.68 | 112 | 20.4 | 18.2 |
| KD-005 | 10 | 5.03 | 0.04 | 0.80 | 9.48 | 0.16 | 1.69 | 80.0 | 0.21 | 0.26 | 5.52 | 0.05 | 0.91 | 0.69 | 142 | 5.22 | 3.68 |

Supplementary Table 5 Summary of experimental data and the fluid-melt partition coefficient of molybdenum.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | |  | *X*CO2 | Salinity (NaCl. wt.%) \* | | | | CMo in fluid (leaching) § | | CMo in fluid (FIs) # | | | | CMo in  Quenched melt | | *D*Mo (leaching)\*\* | *D*Mo (FIs) †† | | | |
|  | |  |  | Supercritical fluid | | Brine | Vapor |  | | Supercritical fluid | Brine | | Vapor |  | |  | Supercritical fluid | | Brine | Vapor |
|  | H2O-CO2 system | | | | | | | | | | | | | | | | | | | |
| C-002 | |  | 0.10 | - | | N.D. | N.D. | 82 | | N.D. | N.D. | | N.D. | 402 | | 0.20 (0.02) | N.D. | | N.D. | N.D. |
| C-003 | |  | 0.20 | - | | N.D. | N.D. | 117 | | N.D. | N.D. | | N.D. | 471 | | 0.25 (0.02) | N.D. | | N.D. | N.D. |
| C-005 | |  | 0.15 | - | | N.D. | N.D. | 155 | | N.D. | N.D. | | N.D. | 456 | | 0.34 (0.04) | N.D. | | N.D. | N.D. |
| C-006 | |  | 0.15 | - | | N.D. | N.D. | 170 | | N.D. | N.D. | | N.D. | 424 | | 0.40 (0.04) | N.D. | | N.D. | N.D. |
|  | H2O-NaCl system | | | | | | | | | | | | | | | | | | | |
| Q-006 | |  | - | 1.1 | | N.D. | N.D. | 185 | | 239 (42.8) | N.D. | | N.D. | 359 | | 0.51 (0.28) | 0.66 (0.33) | | N.D. | N.D. |
| Q-004 | |  | - | 3.9 | | N.D. | N.D. | 254 | | 376 (140) | N.D. | | N.D. | 277 | | 0.92 (0.29) | 1.36 (0.53) | | N.D. | N.D. |
| Q-001 | |  | - | 6.3 | | N.D. | N.D. | 420 | | 402 (50.8) | N.D. | | N.D. | 228 | | 1.84 (0.63) | 1.77 (0.36) | | N.D. | N.D. |
| Q-008 | |  | - | 11 | | N.D. | N.D. | 347 | | 428 (146) | N.D. | | N.D. | 162 | | 2.14 (0.99) | 2.65 (1.30) | | N.D. | N.D. |
| KD-001 | |  | - | 17 | | N.D. | N.D. | 415 | | 461 (144) | N.D. | | N.D. | 145 | | 2.86 (1.25) | 3.18 (1.41) | | N.D. | N.D. |
| KD-002 | |  | - | 21 | | N.D. | N.D. | 432 | | 492 (75.2) | N.D. | | N.D. | 81.0 | | 5.34 (2.57) | 6.08 (2.48) | | N.D. | N.D. |
| KD-003 | |  | - | 44 | | N.D. | N.D. | 290 | | 350 (137) | N.D. | | N.D. | 13.6 | | 21.3 (10.3) | 25.7 (14.0) | | N.D. | N.D. |
| H-002 | |  | - | 6.6 | | N.D. | N.D. | 435 | | 425 (107) | N.D. | | N.D. | 205 | | 2.12 (0.74) | 2.07 (0.9) | | N.D. | N.D. |
|  | H2O-NaCl-CO2 system | | | |  | | | |  | | |  | | |  | | |  | | |
|  |  | | | Starting salinity † | |  | | | | | | | | | | | | | | |
| Q-011 | |  | 0.11 | 7.4 | | 56 | 2.6 | N.D. | | N.D. | 15425 (7750) | | 276 (72) | 189 | | N.D. | N.D. | | 81.8 (41.1) | 1.46 (0.43) |
| Q-014 | |  | 0.15 | 7.8 | | 58 | N.A. | N.D. | | N.D. | 18455 (3094) | |  | 171 | | N.D. | N.D. | | 108 (18.7) |  |
| Q-016 | |  | 0.21 | 7.3 | | 59 | 3.1 | N.D. | | N.D. | 18916 (12130) | | 493 (65) | 145 | | N.D. | N.D. | | 131 (84.1) | 3.40 (1.28) |
| Q-017 | |  | 0.31 | 7.1 | | 62 | N.A. | N.D. | | N.D. | 20023 (2722) | |  | 112 | | N.D. | N.D. | | 179 (69.7) |  |
| KD-005 | |  | 0.30 | 7.4 | | 62 | 2.2 | N.D. | | N.D. | 20773 (6810) | | 492 (72) | 142 | | N.D. | N.D. | | 146 (49.1) | 3.46 (1.01) |
| *Note*:  N.D. = no data.  N.A. = the data were not used because of the large uncertainty.  The data in the brackets ( ) represent 2 sigma standard deviation of the measurements.  \*The salinity was determined microthermometrically and is the average for a set of fluid inclusion assemblages.  †Because of phase separation of H2O-NaCl-CO2 under the experimental conditions, the starting salinity of these experiments is reported.  §This concentration was measured for the quenched fluid from experiments in the H2O-CO2 and H2O-NaCl systems, using a method that involved leaching of the charges with distilled water based on a modification of the method of Keppler and Willie (1991) and analysis by ICP-MS.  #This concentration represents the concentration of Mo in the reacted fluid trapped as fluid inclusions in quartz at the conditions of the experiments involving H2O-NaCl and H2O-NaCl-CO2 and was analyzed by LA-ICP-MS.  \*\*DMo in quenched melts was analyzed by LA-ICP-MS.  ††DMo (leaching) was calculated from CMo in the fluid (leaching)§ divided by CMo in the quenched melt.  §§DMo (FIs) was calculated from CMo in the fluid (FIs)# divided by CMo in quenched melt. | | | | | | | | | | | | | | | | | | | | |

Supplementary Table 6 Parameters and equations used in modeling the Mo extraction efficiency.

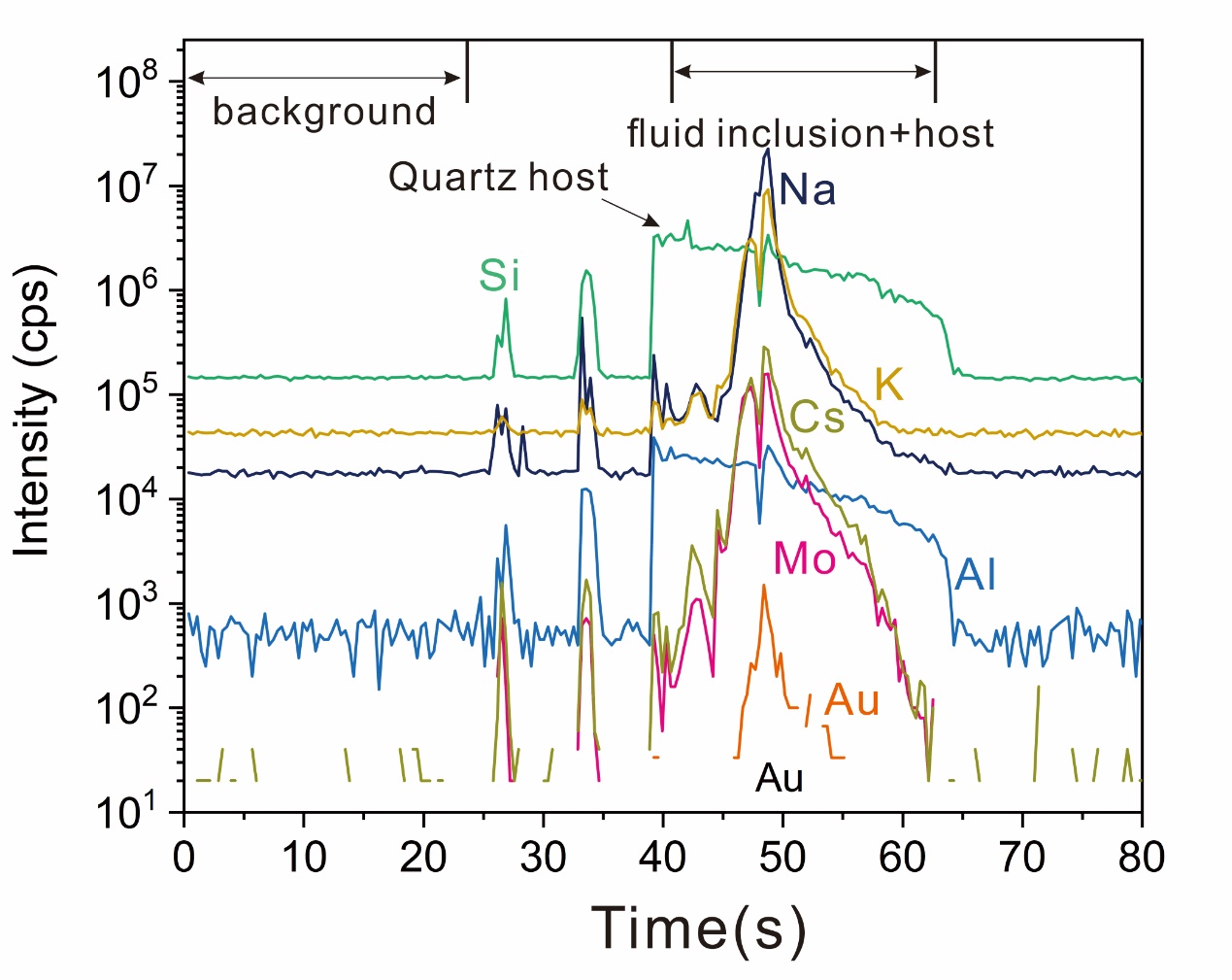
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Initial Parameters | Units | | Value | |  |  |
| Magma volume | km3 | | 100 | |  |  |
| Mo concentration in magma | ppm = 10-6 | | 15 | |  |  |
| H2O (or fluid) content in the magma | wt% | | 5 | |  |  |
| Magma density | ton/m3=g/cm3 | | 2.5 | |  |  |
| Vapor/brine mass ratio |  | | 10 | |  |  |
| Equation | (ref. 14) | | | | | |
| The ratio of exsolved fluid % | The extraction efficiency % | | | | | |
|  | *D*Mobulk = 179\*1/11+2.1\*10/11 | | *D*Mobulk = 81.8\*1/11+1.41\*10/11 | | *D*Mosupercritical fluid = 1.77 (NaCl eq. = 6.3 wt.%) | |
|  | *D*Mobulk | *D*Mobulk calculated to peraluminium melt | *D*Mobulk | *D*Mobulk calculated to peraluminium melt |  | |
| 0 | 0 | 0 | 0 | 0 | 0 | |
| 2 | 30.7 | 16.8 | 17.1 | 8.4 | 3.51 | |
| 4 | 52.4 | 31.0 | 31.5 | 16.3 | 6.97 | |
| 6 | 67.5 | 43.0 | 43.6 | 23.6 | 10.4 | |
| 8 | 78.0 | 53.1 | 53.8 | 30.5 | 13.7 | |
| 10 | 85.3 | 61.6 | 62.3 | 36.8 | 17.0 | |



**Supplementary Figure 1.** Schematic illustration of the experimental design used in our experiments: **a** In the H2O-CO2 system, only the starting glass and solution were loaded in the gold capsule. **b** In the H2O-NaCl and H2O-NaCl-CO2 systems, experiments were conducted using the previously described quartz cylinder containing Rb-bearing fluid inclusions, which were fractured in situ after the experiment had proceeded for up to 7 days. The experimental conditions were then resumed for another 5 days to ensure that the re-healed fluid inclusions trapped the fluid after equilibrium was attained.



**Supplementary Figure 2.** A comparison of the results of the leaching and fluid inclusion methods of fluid analysis for the H2O-NaCl experiments. The error bar illustrates 2 times standard deviation. **a** The concentration of Mo in the leaching solution analyzed by ICP-MS vs. the concentration of Mo in single fluid inclusions analyzed by LA-ICP-MS. Considering that the relative standard deviation of Mo determination in solution by ICP-MS is better than 2-4%, we adopted 4% as the uncertainty of molybdenum concentration in leaching solution measured by ICP-MS. The results demonstrate that the concentration of Mo obtained from the two method is consistent within the uncertainty; the variation between the two sets of data is mostly less than 20%. **b** A comparison of the *D*Mo value obtained using the two methods showing that the results using the two sets of fluid composition data also very consistent.

**Supplementary Figure 3.** The LA-ICP-MS signal obtained from a 20 μm diameter fluid inclusion trapped during experiment Q-011. The brine was trapped in the two-phase region of the NaCl-H2O-CO2 system at 850 ℃, 200 MPa, and contains 15,424 ppm Mo.



**Supplementary Figure 4**. Diagrams showing the variation in the concentration of Mo in the quenched glass after experiments as a function of *X*CO2 and salinity. **a** The concentration of Mo in quenched glass vs. *X*CO2 in the H2O-CO2 system. **b** The concentration of Mo in quenched glass vs. the salinity of the experimental solution in the H2O-NaCl system. (**c**) The concentration of Mo in quenched glass in the H2O-NaCl-CO2 system. The salinity of the brine increased with increasing *X*CO2.

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