The influence of OH in coesite on the kinetics of the coesite-quartz phase transition

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Coesite is an important pressure indicator for metamorphic rocks of ultra-high pressure origin. However, it often does not survive exhumation, but reacts back to quartz. Although it was shown experimentally that hydrogen incorporation in coesite increases with increasing pressure, the few coesite relics, which are found in nature, are "dry". Thus, does the incorporation of hydrogen promote the back-reaction of coesite to quartz during exhumation?
To investigate the influence of intrinsic OH in coesite on the kinetics we investigated the coesite quartz phase transformation by using "dry" coesite with 60 H / 10^6 Si and "wet" coesite with 700 H / 10^6 Si.
Dry coesites were synthesized in a piston-cylinder device apparatus from fine grained quartz powder at 4.0 GPa and 800 ± 5 °C. Hydrous coesite samples were synthesized in multi-anvil apparatus from highly pure SiO_2 with water in excess at 7.5 GPa and 1100 ± 5 °C. The water contents of the starting coesites were quantified by IR spectroscopy [1]. Although we worked hard to avoid OH incorporation, the "dry" coesite still contents 60 ± 10 H / 10^6 Si. The hydrogen coesite of the "wet" coesite sample was 700 ± 100 H / 10^6 Si.
The multi-anvil type X-ray high-pressure/high-temperature system, MAX80 was used for our kinetic studies. In the first series of experiments the transformation kinetic of "dry" coesite was determined in the quartz stability field in the pressure range 2.4-3.0 GPa. The duration of the experiments varies from 60 to 120 min after reaching given pressure and temperature. The counting time for the diffraction pattern was 120 seconds. The transformation kinetic of the "wet" coesite was determined under the same conditions. Counting time for these diffraction patterns was 30–120 seconds. Diffraction patterns were recorded in an energy dispersive mode using white synchrotron X-rays from the storage ring DORIS III. The integrated areas for representative diffraction peaks were obtained by fitting each individual pattern. The peak intensities of the (040) diffraction peak of coesite and (101) diffraction peak of quartz were used to determine the degree of transformation X. Figure1 illustrates time-resolved diffraction patterns for the phase transformation of "dry" coesite to quartz.
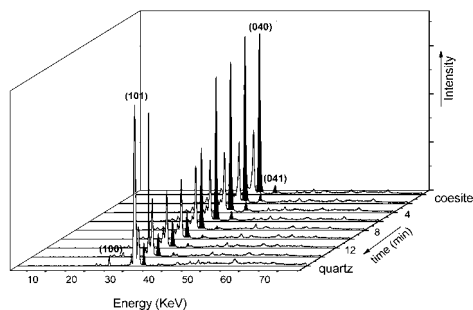

Figure 1: Diffraction patterns versus time during the phase transition coesite-quartz for the dry" coesite at 2.4 GPa and 700 °C.
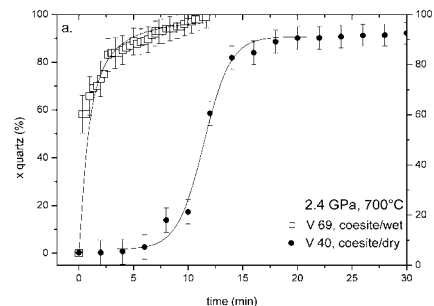

Figure 2: Comparison of transformation versus time curves for the coesite quartz conversion determined by in-situ X-ray diffraction data.

The conversion times for the "wet" coesite were under the same conditions much faster than those of the "dry" coesite (Fig. 2). The kinetics of polymorphic phase transformations can be described by the Avrami equation [2]: $X(t) = 1 - \exp(-kt^n)$ with, $X(t)$ - the volume fraction transformed, t - time, k - rate function and n – a constant parameter which depends on the reaction mechanism. We determined the k and n values from plots of $\ln(-\ln(1-X(t)))$ against $\ln(t)$ (Fig. 3).
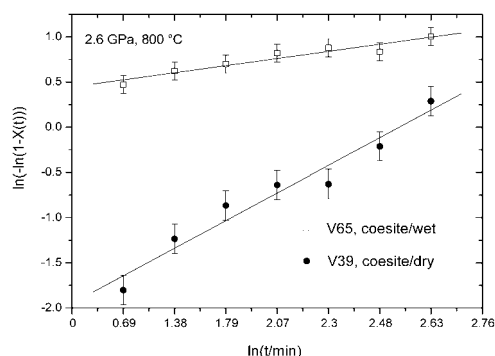

Figure: 3: Comparison of transformation-time data for coesite-quartz transformation for "wet" and "dry" coesite with the conditions 2.6 GPa and 800 °C plotted on a $\ln(-(\ln(1-X(t))))$ against ln (time). The data were fitted with the Avrami equation (solid line).

For the kinetic experiments using "dry" coesite the rate functions k ranged from $1.017 \times 10^{-1}\,\text{s}^{-1}$ to $7.131 \times 10^{-3}\,\text{s}^{-1}$ and the parameters n from 1.17–1.66. The rate functions k and parameters n determined from kinetic experiments using "wet" coesite varies from 1.2–1248 and 0.12–0.40, respectively. Values of n smaller than one are theoretically not possible and may indicate to the weakness of the simple model of Cahn [3, 4]. But, nevertheless the direct comparison of the results of the "wet" and "dry" experiments performed under the same experimental conditions shows that the transformation kinetics of coesite to quartz is several orders of magnitude faster when coesite contains considerable amounts of intrinsic OH.

The transformation kinetics of coesite to quartz is several orders of magnitude faster when coesite contains considerable amounts of intrinsic OH. We highly recommend to determine the influence of intrinsic OH on the kinetics of the phase transitions also in other systems, such as the high-pressure phase polymorphism in Mg_2SiO_4.

References

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