Curious kinetic behavior in silica polymorphs solves seifertite puzzle in shocked meteorite

The evolution of asteroids by collision was the main process of planetary formation in the early solar system. Physical conditions of the collisional process have been recorded in shocked meteorites. Recent findings of various high-pressure silica polymorphs including seifertite, a high-pressure polymorph of silica with the α-PbO_2-type structure, in Martian [1], lunar [2] and other achondritic meteorites are important clues to understanding the shock conditions. However, previous studies faced the problem of the presence of seifertite because this phase is thermodynamically stable at more than 100 GPa [3], which is an unrealistically high pressure condition for shocked meteorites.

In order to solve the seifertite problem, we newly investigated the kinetic aspects of high-pressure transformations of silica by time-resolved X-ray diffraction measurements using a Kawai-type high-pressure apparatus (SPEED-1500) installed at beamline **BL04B1** [4]. The starting materials of synthetic SiO_2 α-cristobalite and reagent-grade SiO_2 quartz powders were first compressed up to ~30 GPa at room temperature, and then heated in 100 K steps up to ~1450 K at a constant load. We kept temperature constant for ~10–50 min at each step and collected diffraction patterns of the sample every 30 to 200 s by the white X-ray energy dispersive method.

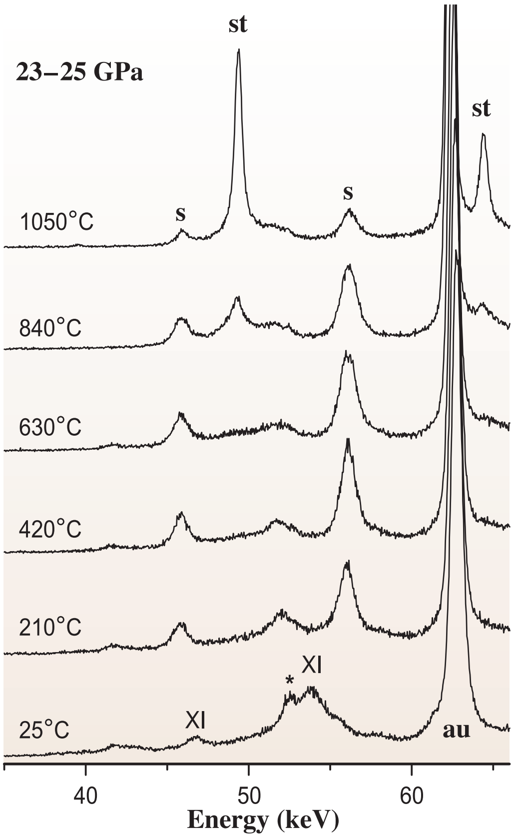

Fig. 1. Changes in X-ray diffraction patterns in cristobalite showing formation of seifertite (s) and stishovite (st) upon heating at 23–25 GPa. Other abbreviations: XI, cristobalite X-I; au, gold pressure marker; *, graphite sample capsule.

Figure 1 shows changes in the diffraction peaks during heating after cold compression in an experiment using α-cristobalite as the starting material. The cold compression of α-cristobalite to around 30 GPa causes high-pressure transitions to cristobalite-II and X-I. When heating the sample at high pressures, we observed the formation of metastable seifertite. Further heating leads to the transformation from seifertite to the stable phase of stishovite. Our experiments suggest that seifertite metastably appears down to ~11 GPa, which is far from its stability field. When using quartz powder as a starting material, we did not observe seifertite formation up to ~25 GPa and 900 K. Stishovite is formed from quartz at much lower temperatures than those in the case of cristobalite.

We quantitatively observed the kinetics of the formation of metastable seifertite and stable stishovite by time-resolved X-ray diffraction measurements. Analysis of the kinetic data (the time dependence of the transformed fraction data) using the Avrami rate equation indicated clear differences in kinetics between seifertite and stishovite formations (Fig. 2). In the case of seifertite formation, the activation energy is very low (~10 kJ/mol) and there is no detectable pressure dependence, implying fast kinetics even at low temperatures because of the diffusionless transformation mechanism from cristobalite to seifertite. On the contrary, the formation of stishovite from seifertite has a relatively high activation energy (~110 kJ/mol) and large activation volume, which is thought to have originated from a diffusion-controlled mechanism.

On the basis of the kinetic parameters obtained in our experiments, we constructed the time-temperature-transformation (TTT) curves for seifertite and stishovite formation (Fig. 3) to discuss the progress of the reaction on short time scales of the shock event in the range from ~0.01 s to ~1 s estimated for Martian and lunar meteorites. Seifertite formation has temperature-insensitive but time-sensitive kinetics, which requires shock durations of at least ~0.01 s to start, even at temperatures of ~2000 K and higher. Completion is difficult within the time scale of shock events. In contrast, stishovite formation is temperature-sensitive, requiring temperatures higher than ~1200–1500 K to start, and can be completed at less than ~2000 K. When considering impact velocities of ~5–10 km/sec and shock durations of ~0.01 sec, the critical size of an impactor that might produce seifertite is estimated to be ~50–100 m. Our finding of the clear difference in kinetics between the metastable seifertite and stable stishovite formations not only solves the seifertite puzzle, but also is potentially capable of being a simple index for the impactor size.

We previously proposed an indicator of shock conditions based on the plagioclase amorphization and crystallization kinetics of high-pressure minerals [5]. When used in combination with the present study, the shock metamorphism observed in achondritic meteorites can be consistently discussed. Thus, the curious kinetic behaviors of silica and plagioclase observed in shocked meteorites can be used as a unique hybrid shock indicator of the collisional history of differentiated parental bodies in the early solar system.

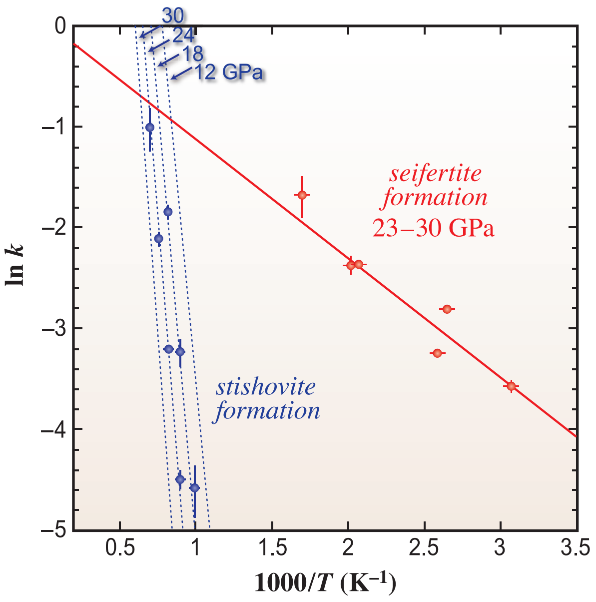

Fig. 2. Temperature dependence of rate constant k. In stishovite formation, the pressure dependence was also observed.

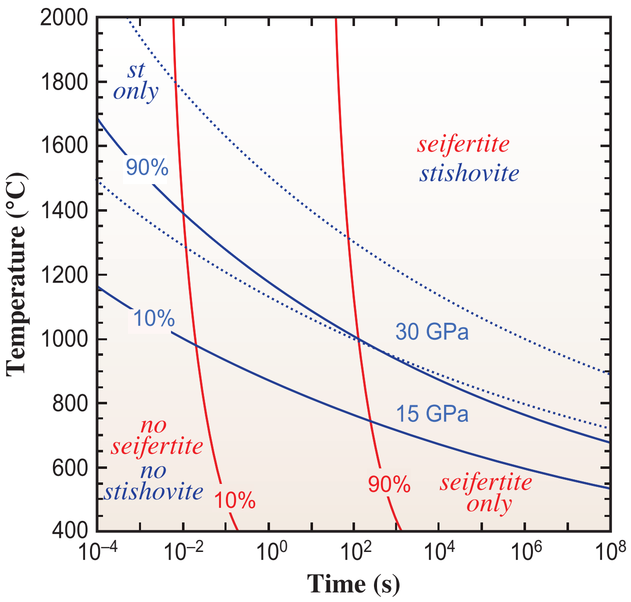

Fig. 3. Time-Temperature-Transformation (TTT) curves constructed on the basis of kinetic parameters determined from Fig. 2.

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References

[1] T.G. Sharp *et al*.: Science **284** (1999) 1511
[2] M. Miyahara *et al*.: Proc. Natl. Acad. Sci. USA **111** (2014) 10939.
[3] M. Murakami *et al*.: Geophys. Res. Lett. **30** (2003) 1207.
[4] *T. Kubo, T. Kato, Y. Higo and K. Funakoshi: Sci. Adv.* ***1*** *(2015) e1500075*.
[5] T. Kubo *et al*.: Nat. Geosci. **3** (2010) 41.