T-T-T DIAGRAM OF SERPENTINE AND SAPONITE, AND ESTIMATION OF METAMORPHIC HEATING DEGREE OF ANTARCTIC CARBONACEOUS CHONDRITES

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Abstract: For the estimation of peak thermal metamorphic degree of phyllosilicates in Antarctic carbonaceous chondrites, heating experiments of serpentine and saponite were carried out. A T-T-T diagram of serpentine for elevated temperature was obtained by heating the serpentine in the Murchison CM2 chondrite in vacuo at different temperatures (250°-1100°C) and for different durations (1 hour to 350 hours). Serpentine decomposed into olivine and enstatite through characteristic transitional structures. First decomposition started at about ~300°C, the transitional structure appears at ca. 400-500°C, and well-crystallized olivine and enstatite appeared above ~750°C. In the T-T-T diagram, a minor time dependence was found. A T-T-T diagram of saponite was obtained in a similar way using terrestrial Fe-saponite. Saponite maintained its structure till about 800-900°C, then decomposition started and finally enstatite was formed. New data on thermally affected phyllosilicates in Yamato(Y)-793321 indicate coexistence of 7 Å unaltered serpentine and a transitional structure. Thermally affected saponite in Belgica(B)-7904 was also documented. Based on the T-T-T diagrams, the peak metamorphic degrees and peak temperatures were estimated in the order of B-7904 > Y-86720 > Y-82162 > Y-793321.

1. Introduction

Two unique carbonaceous chondrites containing thermally metamorphosed phyllosilicates, Yamato(Y)-793321 and Belgica(B)-7904, were first found from Antarctic meteorites (Akai, 1984) and subsequently described in detail by Akai (1988). Later, in two more carbonaceous chondrites Y-82162 and Y-86720 (Akai, 1989; Tomeoka et al., 1989a, b), the thermomorphosed phyllosilicates were also found. These carbonaceous chondrites also have unusual petrographic features (Tomeoka et al., 1989a, b; Zolensky et al., 1989; Bischoff and Metzler, 1991; Ikeda, 1991; Yamamoto and Nakamura, 1990); however, this paper focuses attention only on thermal metamorphism of phyllosilicates.

In these chondrite specimens, saponite and serpentine are the dominant phyllosilicates present (Akai, 1984, 1988, 1989, 1990; Akai and Kanno, 1986; Tomeoka and Buseck, 1988; Tomeoka et al., 1989a, b; Tomeoka, 1990a, b; Zolensky et al., 1989), although additional minor species have been reported (Akai and Kanno, 1986; Tomeoka, 1990b).

It has become important to constrain the nature of thermal events affecting
T-T-T Diagram of Serpentine and Saponite

carbonaceous chondrites. We do not know, for certain, the location of the heating event. Duration and cause of the heating are also unknown although one proposal was given by Miyamoto (1990). In this proposal, heating effect was calculated based on internal heating process of some parent body. Peak temperatures of the thermal metamorphism have been estimated by several different methods; for example, by quantities of organic compound (Shimoyma et al., 1991), labile trace element behavior (Paul and Lipschutz, 1990; cf. Matza and Lipschutz, 1977) or mineralogical aspect (Akai, 1988, 1990; Zolensky et al., 1991), while some estimates disagree in the temperatures.

Time-temperature-transformation (T-T-T) diagrams are important tools for use in mineralogy (Putnis and McConnell, 1980, etc.). Because kinetic factors in reaction are considered in the T-T-T diagram, T-T-T diagrams of saponite and serpentine have a greater utility for estimation of the metamorphic temperature than estimation by fixed time heating experiments.

The main objectives of this paper are to derive T-T-T diagrams of serpentine and saponite based on heating experiments and to apply these T-T-T diagrams to interpretation of metamorphism in the carbonaceous chondrites. I also give new HRTEM data on phyllosilicates in Y-793321 and B-7904, which will become an important key to the estimation of their metamorphic degree.

2. Specimens and Analytical Procedures

Specimens used in heating experiments were the serpentine-bearing Murchison CM2 chondrite and terrestrial saponite from the Green tuff region in Japan (Yoshimura et al., 1975); the both are the same specimens used in the heating experiments by Akai (1990). Heating experiments were carried out in vacuo because natural process of heating in carbonaceous chondrites is estimated to have occurred most probably in vacuo. Powdered specimens were heated in vacuo in silica glass tubes at \( \sim 10^{-3} \sim 10^{-3} \) Torr at temperatures of 250\(^\circ\)C to 1100\(^\circ\)C, and for varying durations (1 to 350 hours). Matrices of the specimens were extracted and were thinned by ion bombardment, as in Akai (1988). Heated specimens were examined by transmission electron microscopy (TEM) and electron diffraction (ED) and analytical electron microscopy (AEM), all using JEM-200 CX operated at 200 kV. AEM analysis was carried out with a beam diameter of 1500\(-4000\) Å.

Antarctic carbonaceous chondrites, Y-86720 and Y-82162 supplied form NIPR (cf. Akai, 1990) were ion-thinned and reexamined by HRTEM and AEM.

3. Results and Discussions

3.1. Heating experiments and T-T-T diagrams

In the experiments with Murchison, ED patterns and lattice images of serpentine were observed to change significantly with temperature. Figure 1 shows some typical changes in TEM images and corresponding ED patterns of serpentine in elevated temperatures. At low temperatures, (for example, at 300\(^\circ\)C for 1 h (Fig. 1a), at 250\(^\circ\)C for 330 h and 300\(^\circ\)C for 18 h) dim spotty portions in 7 Å lattice images
Fig. 1. Some typical EM images and ED patterns of serpentine in the Murchison chondrite heated in the following conditions:
(a) 300°C, 1h. (b) 400°C, 1h. (c) 700°C, 48 h.
In (b), coexistence of serpentine structure and the transitional structure is noted.
Fig. 2. Some typical EM images and ED patterns of terrestrial Fe-saponite heated at the following conditions;
(a) 750°C, 168 h. (b) 800°C, 168 h. (c) 1000°C, 1 h.
In (c), enstatite with disordered structure is noted.
sometimes appeared or no change was observed. The spotty portions are considered to indicate initiation of decomposition. No significant changes in ED pattern were noted at this stage.

At slightly higher temperatures (for example at 400°C for 1 h (Fig. 1b), also at 300°C for 168 h, at 350°C for 1 h, at 350°C for 20 h, at 350°C for 48 h, at 400°C for 20 h, at 400°C for 24 h, and at 450°C for 1 h), characteristic diffuse diffraction halos of 2.4–3.6 Å range and extra diffuse spots of 9–13 Å appeared in

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**Fig. 3.** T-T-T diagram of serpentine for elevated temperature. Lines A, B and C in the figure indicate the following:

A: Beginning of decomposition (appearance of diffraction halos).
B: Disappearance of 7Å layer structure (with diffuse olivine spots).
C: Disappearance of diffraction halos (with olivine spots).
ED patterns (Fig. 1b). Similar ED patterns were observed in thermally affected phyllosilicates in Y-793321 by Akai (1988). The extra spots were considered to be due to transitional structure in transformation from serpentine to olivine. Here, the term of transitional structure is used for the structure of 'transitional stage' proposed by Brindley and Zussman (1957), which corresponds to characteristic low-angle broad peak in X-ray diffractometer trace. However, it is not yet clarified whether it is stable phase or not, and its structural detail is not disclosed although HRTEM photographs suggest some layered structure observed in Y-793321.

At further higher temperatures (for example, at 700°C for 48 h (Fig. 1c), at 400°C for 48 h, at 450°C for 15 h, at 450°C for 24 h, at 500°C for 1 h, at 500°C for 24 h, at 500°C for 48 h, at 600°C for 1 h, at 600°C for 48 h, at 700°C for 1 h, at 700°C for 24 h, and at 800°C for 1 h), diffuse olivine spots changed to sharp

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![T-T-T Diagram of Serpentine and Saponite](image)

**Fig. 4.** T-T-T diagram of Fe-saponite at elevated temperature. Lines in the figure indicate the following changes:

- **A**: Start of decomposition.
- **B**: Disappearance of layer structure and appearance of enstatite.

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spots. Halo diffraction became faint or disappeared (Fig. 1c).

Above those temperatures (at 750°C for 168 h, at 800°C for 24 h, at 800°C for 48 h, at 900°C for 1 h, at 900°C for 24 h, at 900°C for 48 h, at 950°C for 72 h, at 1000°C for 1 h, and at 1100°C for 1 h) enstatite finally appeared.

Fig. 5.
Original serpentine in Murchison shows compositional fluctuations. Especially, the Fe/Mg ratio of every original serpentine grain in Murchison was often variable. Thus, taking a lot of photographs of TEM and ED patterns, and AEM spectra of the specimens, general tendency of thermal effect on phyllosilicates under some condition was estimated. The thermal effects on phyllosilicates with slightly different compositions did not seem to differ so significantly: even if the phyllosilicates did not have the same Fe/Mg ratio the thermal effects were not much different.

Figure 2 shows the systematic changes observed in saponite. In saponite, clear transitional structures were not formed and at high temperatures above 800~900°C (for example, heating at 800°C for 168 h (Fig. 2b) and also heating at 850°C for 14 h, at 850°C for 96 h, and at 900°C for 1 h) it became degraded and showed ring-like diffraction in ED patterns. In heating saponite at higher temperatures (for example, at 1000°C for 1 h (Fig. 2c), at 950°C for 1 h, at 950°C for 72 h, at 1000°C for 13 h, at 1050°C for 1 h, and at 1100°C for 1 h) enstatite was observed.

Summarizing all the results of the heating experiments, T-T-T diagrams were derived for both serpentine and saponite (Figs. 3 and 4). Several provisional
Fig. 6. ED pattern and dark field EM images of incompletely transformed serpentine with transitional structure in Y-793321.
(a) BF (Bright Field) EM image of the specimen. (b) typical ED pattern and its explanation: Subscripts o and s represent olivine and serpentine, respectively. ○: olivine; ○: serpentine; —: streaks due to stacking disorder in serpentine; ●: broad spots which may be due to transitional structure. Broad ring halo (2.4–3.6 Å region) is not shown in the explanation figure. (c) DF (Dark Field) image by diffuse olivine spot. Small spotty pattern is found. (d) DF image by dim extra spot (9–13 Å) which may correspond to transitional structure. Diffuse lattice-like image is found. (e) DF image by ring diffraction halo. Very fine homogeneously distributed phases are characteristic.
Fig. 6.
Fig. 7 a, b. EM images and the corresponding ED patterns of thermally affected saponite in B-7904. Selected areas for ED pattern are a little wider than the figures shown. AEM spectra for areas a little wider than the figures shown are inserted. Ca has probably originated from adjacent minerals.
boundaries dividing different products and ED patterns were drawn on these diagrams (Figs. 3 and 4). As shown in Figs. 3 and 4, structural changes documented here have a minor time dependence. A small gap exists between the results of heating for short duration (1 h) and those for longer duration. Changes noted for the Murchison serpentine assemblage can be divided into four types of 250~1100°C. Saponite assemblage cannot be so divided. These diagrams can well be applicable to those for such short time reactions. Rough estimation may also be possible for more long time processes because time dependence seems to be small except for heating for 1 hour in Figs. 3 and 4.

3.2. Additive data on thermally-affected phyllosilicates in Y-793321 and B-7904

Details of structures and textures of the phyllosilicates are essential for the estimation of metamorphic heating degree. Phyllosilicates in Y-793321 and B-7904 have been reported by AKAI (1988) but some new important data were found in this study by HRTEM. In Y-793321, HRTEM images of coexisting transitional structures and remnant serpentine were newly found, which are strongly indicative of its heating degree (Figs. 5a and 5b). Furthermore, a TEM image suggesting a type of the start of decomposition, i.e. lamella-like transformation structures, was also found in Y-793321 (Fig. 5b). In Fig. 5b, slightly wider lattices with light contrast are inserted in the characteristic 7 Å lattice spacing of serpentine. It is estimated in comparison with typical lattice images that portions with the wider lattice spacing may be transitional structure in decomposition from serpentine to olivine. Any peculiar contrast was not found and then no strain may be present near the lamellae.

Dark field TEM images of the transitional structure of the thermally affected phyllosilicates in Y-793321 were also taken in this study (Fig. 6). In the dark field TEM images of phyllosilicate grains in Y-793321, shapes and sizes of the phases corresponding to ED patterns were characterized, and the images suggest a transformation mechanism. That is, extra spots in ED patterns correspond to a transitional structure with characteristic 9~13 Å lattice, diffuse olivine spots in ED patterns to spotty small domains, and diffraction halos to very small homogeneously distributed materials. In B-7904, HRTEM images of thermally affected saponite are shown in Fig. 7. More than four hundred EM photographs were taken over for wide area of the specimen. However, clear phyllosilicate lattice images were never taken; only rare vague lattice image of thermally degraded saponite grains was found. Figures 7a and 7b show EM images of thermally affected saponite. Characteristic ED patterns and TEM images resemble those of heated saponite (800~900°C). This degree corresponds to high temperature based on the present T-T-T diagrams. ZOLENSKY et al. (1989) and TOMEOKA (1990a) suggested the presence of both saponite and serpentine in B-7904 but not clear serpentine grains were confirmed. Their "serpentine" may be completely transformed to olivine; this suggestion is consistent with the T-T-T diagram of serpentine.

3.3. Inferred decomposition process of serpentine structure

Inferred decomposition process of serpentine can be estimated as follows; at
Fig. 8. Presumed reaction process of serpentine and saponite at elevated temperatures. Estimated temperature scale is also inserted. This reaction scheme on serpentine is fundamentally based on that by Brindley and Hayashi (1965). However, in this scheme, transitional structure is placed in the first stage of decomposition, because transitional structure was observed by HRTEM to be derived directly from serpentine structure.
the first stage, decomposition may start in mottled or lamellar portions. Through this process, serpentine structure may change to transitional structure whose detail is not yet known but may have some layer structure with 9–13 Å repeating period. Then, at nucleation sites, olivine of very small size or disorganized structure which corresponds to broad diffraction spots in ED patterns may grow. The observed data suggest coexistence of such transitional structure, remaining serpentine structure and newly formed olivine structure. Thus, the reaction may be heterogeneous process. Then, olivine structure is finally completed, transitional structure disappears and crystallinity goes well.

Decomposition process of saponite cannot be clearly distinguished by several stages but probably through some degraded state, enstatite soon crystallizes. Thus a presumed decomposition process can be summarized as in Fig. 8. Thermal transformation process of serpentine has been discussed by many investigators (BRINDLEY and ZUSSMAN, 1957; BRINDLEY and HAYASHI, 1965; BALL and TAYLOR, 1963; SOUZA SANTOS and YADA, 1983; AKAI, 1990). A donor and acceptor region model was proposed by BRINDLEY and HAYASHI (1965). They suggest that in this model, decomposition and nucleation occur in two different domains; donor region in which decomposed materials are produced and acceptor region in which crystallization occurs by receiving materials from donor regions. In the process of serpentine decomposition, nucleation sites of olivine clearly correspond to the acceptor region.

Temperature estimations are also given in Fig. 8. In carbonaceous chondrites which contain both serpentine and saponite, temperature estimation using this figure will be more reliable.

### 3.4. Estimation of peak temperature in thermal metamorphism based on T-T-T diagram

According to AKAI (1990) matrix phyllosilicates in both Y-86720 and Y-82162 might be serpentine and saponite. These phyllosilicates were strongly affected by thermal metamorphism. The serpentines were transformed almost completely to olivine (Y-86720) or to transitional structure (Y-82162). Thus, the degree of thermal metamorphism in Y-86720 was considered to be higher than in Y-82162.

Combining all the data on phyllosilicates and their thermally changed products in Y-793321, Y-86720, Y-82162, and B-7904, and the T-T-T diagrams obtained

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<th>B-7904</th>
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in this study, the degree of thermal metamorphism in each specimen can be roughly estimated as in Table 1. Temporary temperature scales are suggested for both short- and long-duration reactions although much longer duration experiments may be necessary for the estimation of long duration reaction.

On the other hand, ZoLENSKY et al. (1991) estimated the temperature of thermal metamorphism in Y-86720, Y-82162, and B-7904 to be probably 400 to 500°C based on heating experiment of the Murchison chondrite in an anoxic (10^−4 bars H₂) environment. PAUL and LIPSCHUTZ (1990) have also suggested based on labile trace element measurements, that the peak temperature of thermal metamorphism in these three meteorites may be in the range of 600~700°C. The estimation of relative temperatures of thermal metamorphism among the four Antarctic carbonaceous chondrites Y-793321, B-7904, Y-82162, and Y-86720 is not uniquely determined. For example, based on the amount of organic compounds SHIMOYAMA et al. (1991) suggest the order of Y-86720>B-7904≈Y-793321>Y-82162> for peak metamorphic heating. PAUL and LIPSCHUTZ (1990) suggest the order of Y-86720>Y-82162>B-7904.

Discrepancies are still present in the temperature estimations. Estimations by different methods may be based on different assumptions and/or different experimental conditions. Specimens used in the experiments might be different because of their heterogeneities. The results of this study are based purely on mineralogical evidence with assumptions that precursor phyllosilicates were normal hydrous silicates. I believe that the estimation in this study may be closest to the conditions of the natural processes. Further comparative studies, however, may be necessary, employing extensive sampling and longer experimental durations.

Acknowledgments

The author wishes to acknowledge Prof. T. YOSHIMURA for kindly supplying the saponite sample and encouragement in this study. He also thanks the National Institute of Polar Research for providing the meteorite samples, Y-793321 and B-7904, and Dr. M. E. ZOLENSKY for his helpful and critical reading of the manuscript.

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259–275.


(Received September 3, 1991; Revised manuscript received January 13, 1992)