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MINERALOGICAL EVIDENCE OF HEATING EVENTS IN ANTARCTIC CARBONACEOUS CHONDRITES, Y-86720 AND Y-82162

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Abstract: Antarctic carbonaceous chondrites, Y-82162 and Y-86720 were examined by transmission electron microscopy. Matrix phyllosilicates in both meteorites are probably serpentine and saponite. There is evidence that these phyllosilicates were affected by thermal metamorphism. The serpentine was almost completely transformed to olivine or an intermediate phase between serpentine and olivine. The degrees of thermal metamorphism in Y-86720, Y-82162 and Y-793321 were compared, and heating experiments of terrestrial saponite and Murchison CM chondrite were also carried out for detailed comparison. Based on these observations and experiments, estimated degrees are as follows: Y-86720 > Y-82162 > Y-793321.

1. Introduction

Among a large number of Antarctic meteorites discovered, representatives of hitherto rare or unknown types are sometimes found. Y-86720 and B-7904 have been previously classified into the CM group (KOJIMA *et al.*, 1984; SKIRIUS *et al.*, 1986; AKAI, 1988; TOMEOKA *et al.*, 1989b) and Y-82162 has been classified into the CI group (KOJIMA and YANAI, 1987; TOMEOKA *et al.*, 1989a; ZOLENSKY *et al.*, 1989a). However, oxygen isotopic characteristics of these meteorites are CI-like (MAYEDA *et al.*, 1987; CLAYTON and MAYEDA, 1989), and details of mineralogy and chemistry of these meteorites are different from those of ordinary CM or CI chondrites (TOMEOKA, 1989; ZOLENSKY *et al.*, 1989b). TOMEOKA *et al.* (1989a, b) studied Y-86720 and Y-82162 by TEM and suggested that they have been thermally metamorphosed.

Recent high-resolution transmission electron microscopy (HRTEM) studies have shed light on the characteristics of phyllosilicates in CM and CI carbonaceous chondrite matrices (MACKINNON and BUSECK, 1979; MACKINNON, 1982; MACKINNON and ZOLENSKY, 1984; MCKEE and MOORE, 1979; AKAI, 1980, 1982; AKAI and KANNO, 1986; BARBER, 1981, 1985; TOMEOKA and BUSECK, 1985, 1988); the matrices of CM chondrites are, in general, characterized mostly by serpentines, and the matrix of the Orgueil CI chondrite is composed of heterogeneous mixture of saponite and serpentine.

On the other hand, two unique carbonaceous chondrites in which constituent phyllosilicates were thermally metamorphosed have already been reported (AKAI, 1988). In Y-793321 and B-7904, matrix phyllosilicates might have experienced heating events at a late stage in the process of the meteorites before their atmospheric entry

to the Earth.

Thus, heating event in carbonaceous chondrites is now becoming an interesting problem to be solved in connection with their origins and processes.

The first objective of this paper is to report mineralogical evidence of a heating event from phyllosilicates of Y-86720 and Y-82162. The second objective is to examine the degrees of thermal metamorphism in these meteorites and Y-793321 based on comparative heating experiments of the Murchison CM chondrites and terrestrial saponite.

2. Specimens and Experimental Methods

Specimens available for the present study are relatively small (Y-86720, 0.223 g; Y-82162, 0.088 g). Specimens for EM observations were extracted from a polished thin section and were thinned by ion bombardment. General mineralogy and petrology of Y-86720 and Y-82162 are reported by TOMEOKA *et al.* (1989a, b).

A JEM 200CX transmission electron microscope (combined with an energy dispersive X-ray detector, TN-2000), operated at 200 kV, was used.

The electron beam was usually focussed to a diameter of *ca.* 1500–4000 Å for analysis in TEM mode. The size of the X-ray source is approximately of the order of the electron beam diameter for a thin specimen and an accelerating voltage of 200 kV. Isolated single grains in ion-thinned specimens were selected for analysis but some analyses could not escape from slight contamination by neighbouring grains. Quantitative analysis was carried out on the basis of the CLIFF and LORIMER (1972) thin film technique using K-factors experimentally determined from synthesized glass standards.

3. Results and Discussion

3.1. EM examination of Y-86720 matrix

Y-86720 matrix contains almost amorphous Fe-rich materials between the interstices of the elongated mineral grains (Fig. 1a); they may be ferrihydrite (TOMEOKA *et al.*, 1989b). Small grains of Fe-sulfides (troilite or pyrrhotite), Ca-carbonate, magnetite, kamacite, and taenite also occur in the matrix. Figure 1b shows Ni-iron (I) and Ca-carbonate (C) grains in the matrix. Ni-iron is kamacite. Figure 2 shows one of typical textures of matrices in Y-86720. The compositions of the grains in Fig. 2 by AEM are shown in Table 1 (analysis no. 114) although this composition may be slightly contaminated with inclusions of some other mineral grains. This composition is fundamentally similar to that of serpentine. Figure 3 shows another view of the matrix where irregularly shaped porous grains are common. Table 1 shows the composition of these porous grains (anal. no. 117). The composition is similar to that of serpentine although it is also contaminated. Their electron diffraction (ED) patterns show little evidence of transformation from serpentine to olivine but show almost completely transformed features. So, these grains are identified to be mostly olivines and might have been transformed from serpentine.

Figure 4 shows elongated grains. The composition from this area is shown in Table 1 (anal. no. 126) and is a Fe-rich saponite composition. D-spacing of the faint

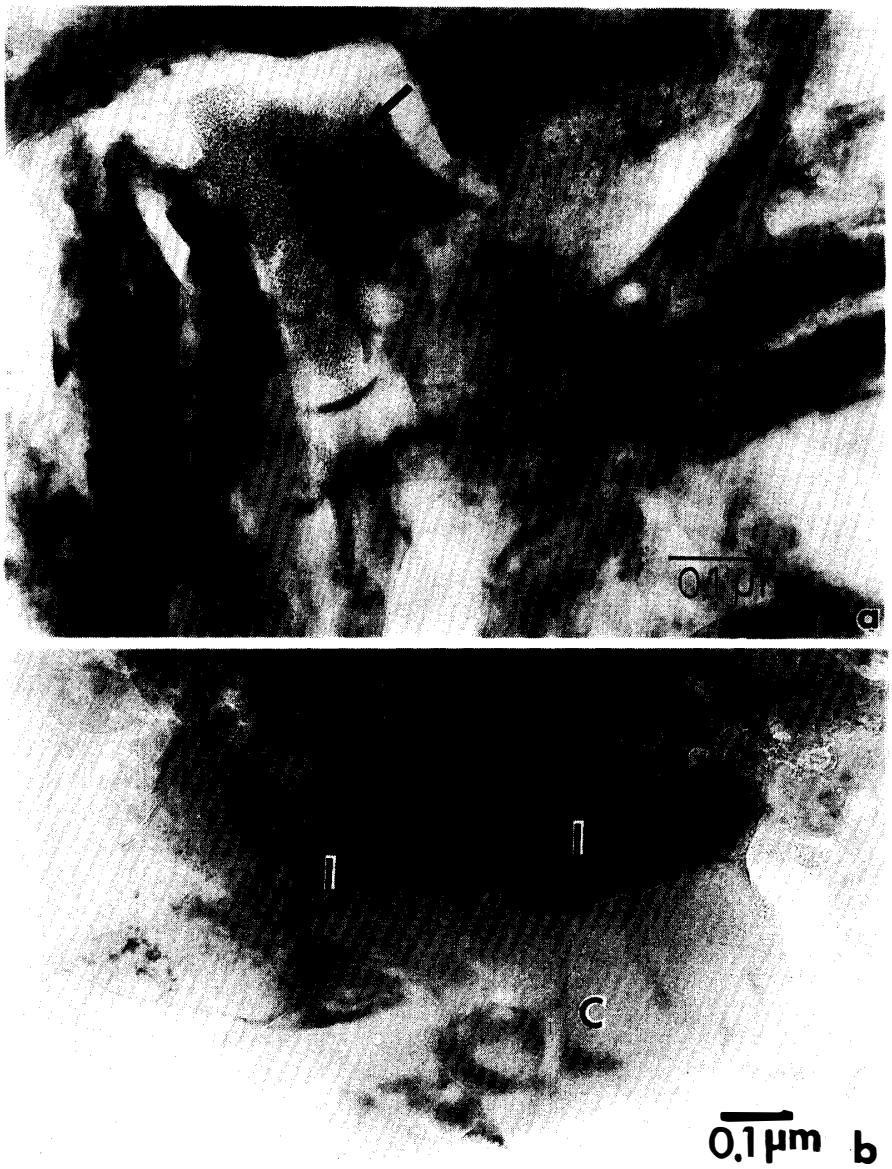

Fig. 1. EM image of Y-86720. a: EM image showing matrix texture. Spongy iron-rich materials are present in the interstices of elongated grains. It may be ferrihydrite, according to TOMEOKA *et al. (1989b). b: Small Ni-iron (I) and Ca-carbonate (C) grains in the matrix.*

lattice image partly resolved is *ca.* 9.5 Å which may be due to remaining saponite. In the figure, small rounded grains scattering are characteristic of this sample. As described below, such rounded grains are characteristic of saponites heated in air for an hour at above 900°C. These grains may be just transforming partly.

3.2. EM examination of Y-82162

Figure 5 shows various matrix textures of Y-82162. The AEM result (anal. no. 5) of the phase shown in Fig. 5a is given in Table 1. It was estimated based on their morphology and AEM analysis that they were once serpentine. Small grains of Mg, Fe-carbonate, Fe-sulfide, dolomite, kamacite and taenite are present among the ser-

Fig. 2.

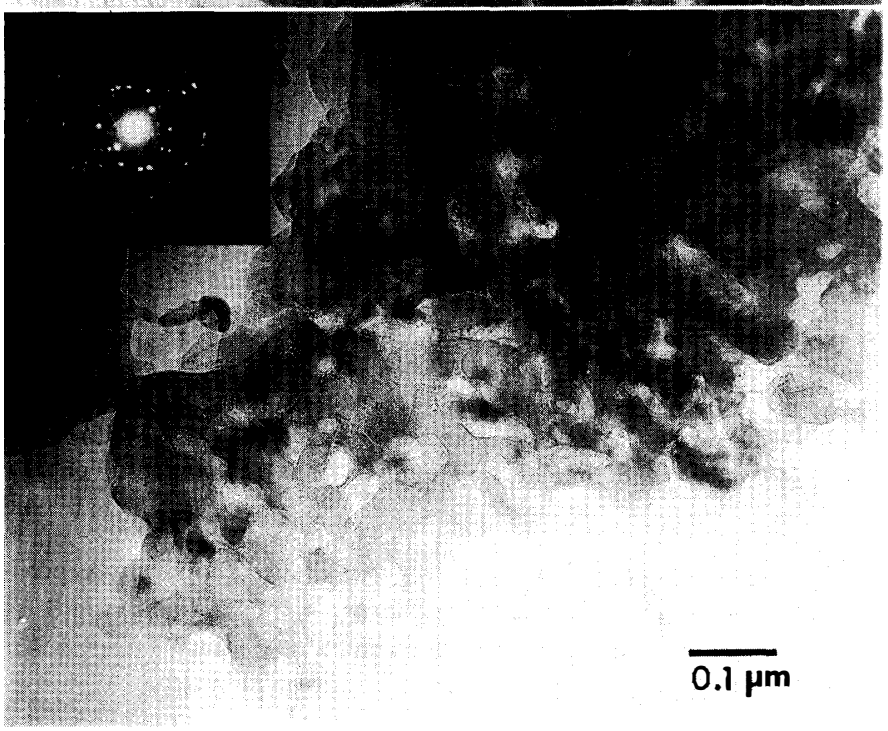

Fig. 3.

Fig. 2. EM image of Y-86720 showing matrix textures. Elongated and irregularly shaped grains might be pseudomorphs after phyllosilicates. The composition (analysis no. 114) of this area is shown in Table 1.

Fig. 3. EM image of Y-86720. Irregularly shaped porous olivines in Y-86720. AEM results from this area are calculated and shown in Table 1 (anal. no. 117).

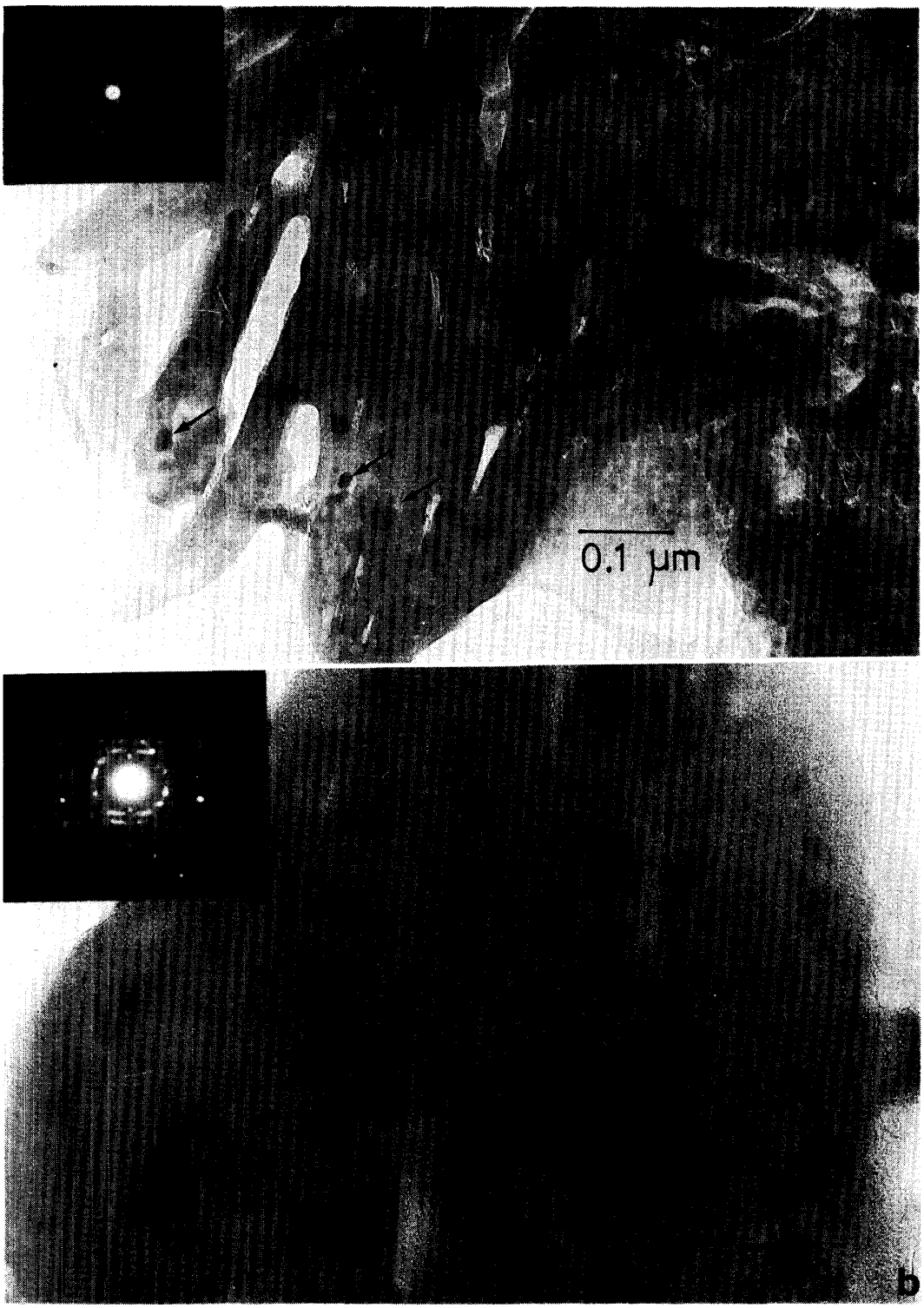

Fig. 4. a: EM image of saponite affected by heating (Y-86720). Spotted morphology (arrows) are characteristic of heating.
b: Lattice image of the saponite in Y-86720. ED pattern is inserted. AEM results are shown in Table 1 (anal. no. 126). Spotted morphology is designated by arrows.

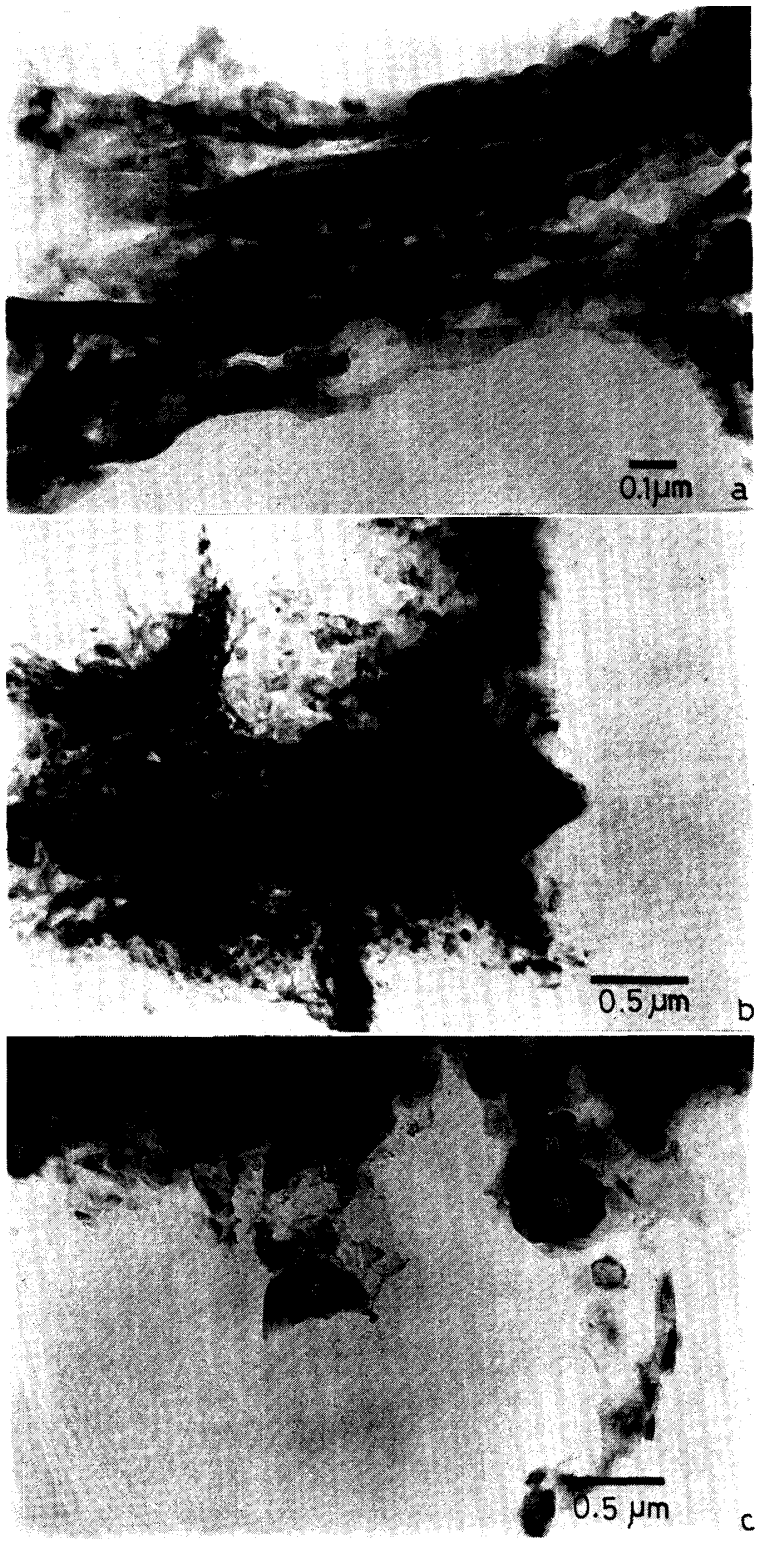

Fig. 5. Low magnification EM image of Y-82162. a: Elongated and irregularly shaped mineral grains in Y-82162. Corresponding AEM analysis is shown in Table 1 (anal. no. 5). b: Small grains of Fe-sulfides (T) and Ni-iron (I). c: Small grains of Mg, Fe carbonate (M) and sulfide (T).

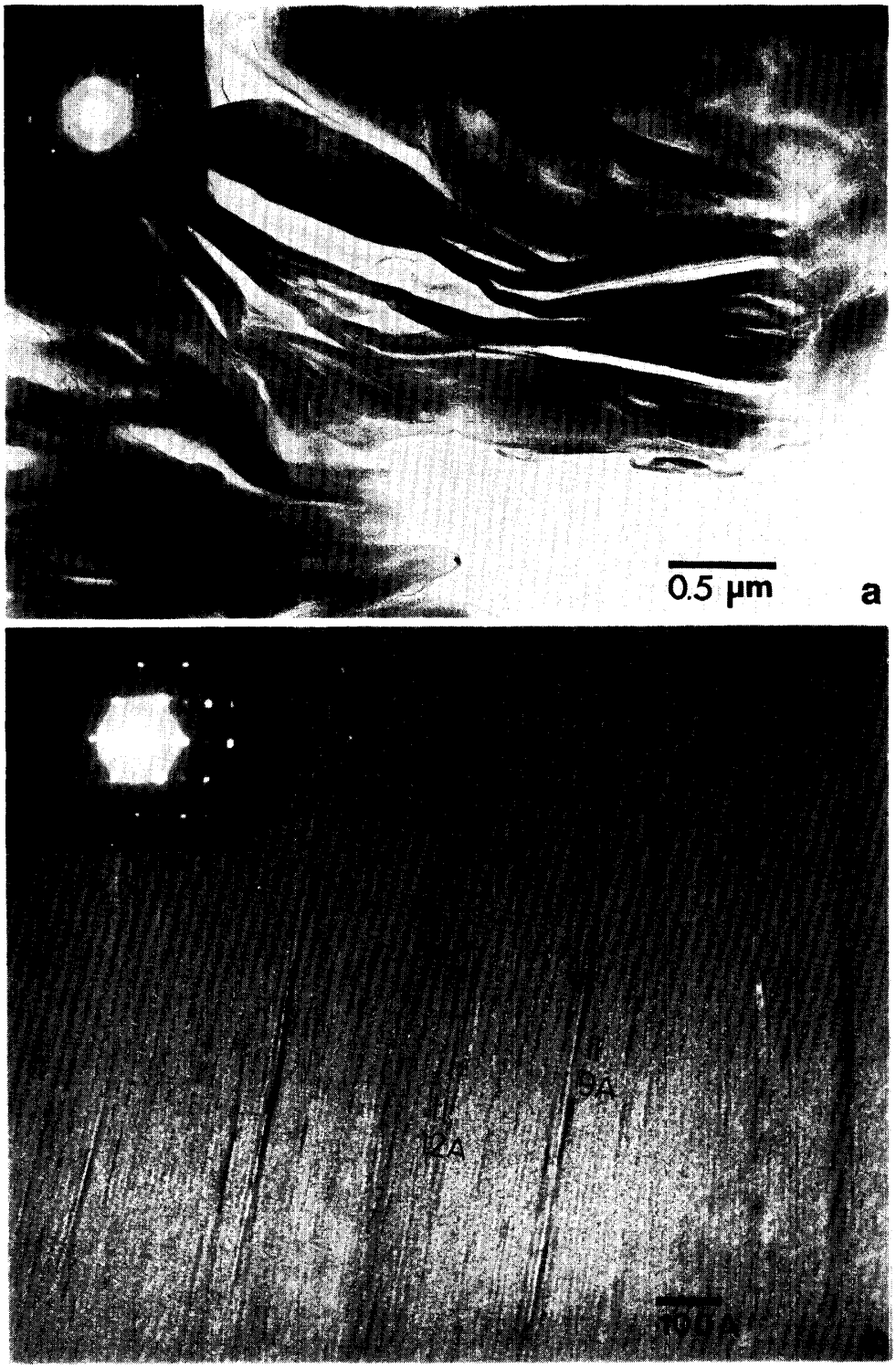

Fig. 6. a: Low magnification EM image of Y-82162 matrix showing flaky pseudomorphs after phyllosilicates. The result of AEM is shown in Table 1 (anal. no. 24).
b: Lattice image of a part of Fig. 6a. The lattice image of intermediate structure in transformation from serpentine to olivine structure. The inserted ED pattern more clearly indicates the intermediate features. It is similar to that found in Y-793321.

Fig. 7. a: Low magnification EM image of saponite in Y-82162 matrix.
b: Intermediate magnification EM image of saponite in Y-82162. In the ED pattern and lattice image a faint ~9.5Å dehydrated saponite spacing is recognized. The resultant AEM anlysis (anal. no. 8) is shown in Table 1.

Table 1. Compositions of thermally affected phyllosilicates in Y-86720 and Y-82162 analyzed by AEM.

	Y-86720				Y-82162				
Anal. no.	114	119	117	126	5	24	8	(1)	Ter. sap.
Na_2O	0.0%	2.1	1.7	3.4	1.4	3.9	1.7	2.2	0.1
MgO	48.2	28.5	39.4	20.5	34.5	30.7	20.2	21.5	19.6
Al_2O_3	0.7	3.5	1.6	4.1	1.2	4.3	4.5	6.0	7.2
SiO_2	43.7	44.4	38.8	49.1	37.4	41.3	48.8	47.9	49.6
K_2O	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.4	0.1
CaO	0.3	0.2	0.3	3.3	0.0	0.2	0.5	0.4	3.7
TiO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cr_2O_3	0.1	0.3	0.4	1.2	0.4	1.9	0.7	0.7	0.0
MnO	0.3	1.2	0.7	0.0	0.2	0.2	0.4	0.2	0.1
FeO	6.5	19.8	17.1	18.4	24.7	17.5	23.2	20.7	19.5
Total	99.8	100	100	100	100	100.1	100	100	99.9
Ox. T	7	7	7	11	7	7	11	11	11
Na	0.000	0.180	0.147	0.454	0.125	0.336	0.228	0.294	0.013
Mg	3.018	1.886	2.627	2.105	2.382	2.039	2.090	2.209	1.988
Al	0.034	0.183	0.084	0.332	0.065	0.225	0.368	0.487	0.577
Si	1.835	1.971	1.735	3.382	1.732	1.840	3.388	3.301	3.374
K	0.000	0.000	0.000	0.000	0.011	0.005	0.000	0.035	0.008
Ca	0.013	0.009	0.014	0.243	0.000	0.009	0.037	0.029	0.269
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.003	0.010	0.014	0.065	0.014	0.066	0.038	0.038	0.000
Mn	0.010	0.045	0.026	0.000	0.007	0.007	0.023	0.011	0.005
Fe	0.228	0.735	0.639	1.060	0.956	0.652	1.347	1.193	1.109
fm	0.07	0.28	0.20	0.33	0.29	0.24	0.39	0.35	0.34

Ter. sap.: Terrestrial Fe-saponite (*cf.* YOSHIMURA *et al.*, 1975).
Ox. T: oxygen total
Ox. T=7 for serpentine or similar phyllosilicate compositions.
Ox. T=11 for saponite or similar phyllosilicate compositions.
fm=Fe/(Mg+Fe).

pentine grains. Ni-iron (I) and troilite (T) are often associated in the neighboring regions (Fig. 5b, c). Figure 6a shows another low magnification EM image clearly indicating pseudomorph of flaky phyllosilicates. The AEM result (anal. no. 24) suggests that it has compositions close to serpentine. Figure 6b is a high resolution EM image of a part of Fig. 6a. The lattice spacings of this area are 9 Å to 12 Å, which are similar to characteristic lattice spacings found in Y-793321 although details are different. The ED patterns with diffraction halos suggest the presence of an intermediate phase in transformation from serpentine to olivine.

The degree of transformation is a little higher than that found in Y-793321 because olivine spots in the ED pattern are sharper than in Y-793321 although this ED pattern also has some remaining diffraction halos. Figure 7 shows flaky and elongated grains in Y-82162. Such flaky and elongated grains do not occur widely. Their compositions (anal. nos. 8 and 1) are close to those of saponite. The faint fringes shown in Fig. 7b have a spacing of ~9.5 Å, which may correspond to that of dehydrated saponite. Small rounded grains scattering could not be observed very clearly.

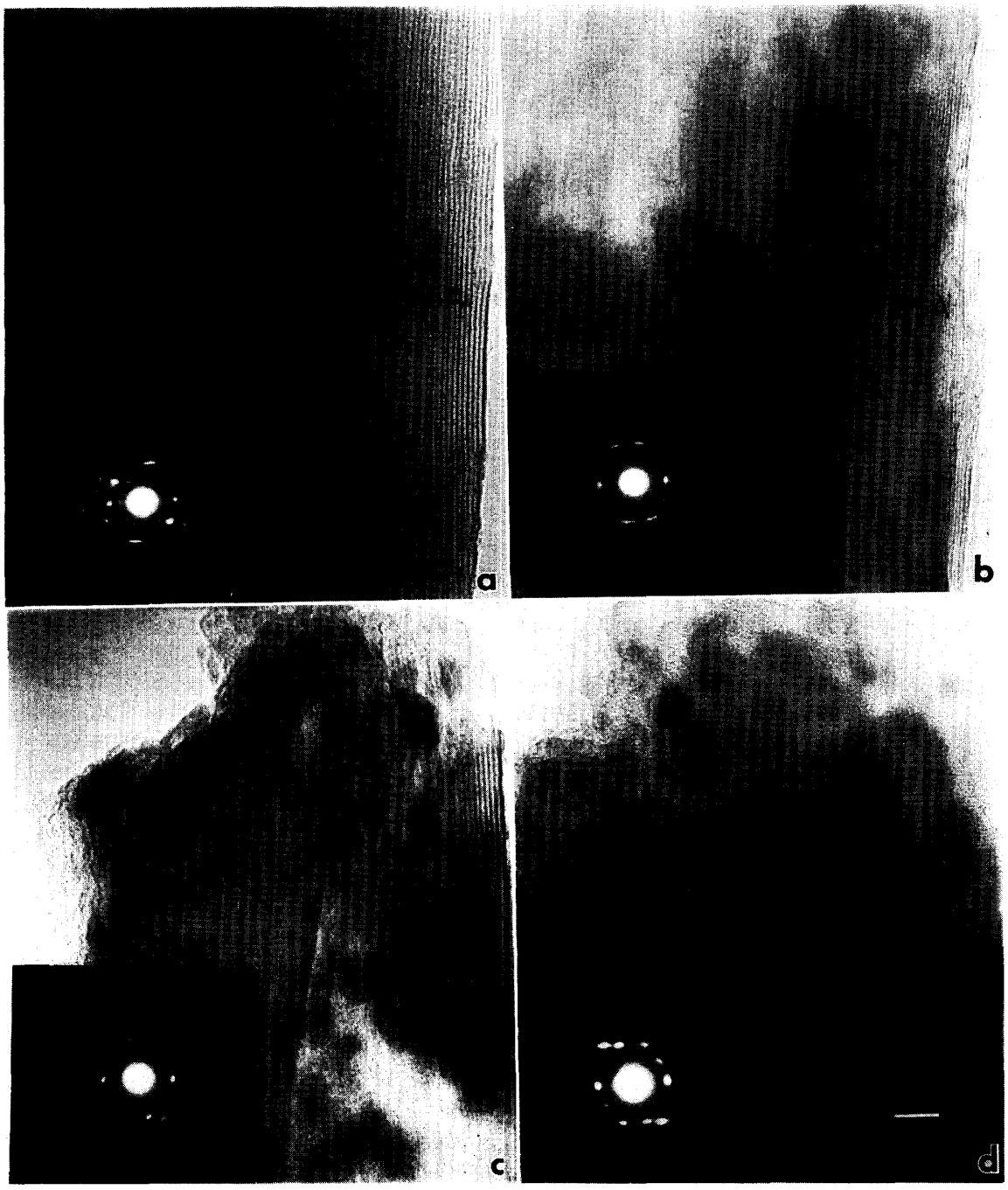

Fig. 8. EM images of heated terrestrial Fe saponites whose composition is shown in Table 1 (Ter. sap.). Saponites were heated (a) in air for an hour at 800°C, (b) in vacuo for 48 hours at 800°C, (c) in air for an hour at 900°C and (d) 1000°C.

Based on the ED patterns and the EM images, the degree of transformation of the phyllosilicates in Y-82162 may be lower than that of Y-86720, and it may be higher than that in Y-793321.

3.3. Heating experiments of saponite and Murchison CM chondrite

To estimate the degree of thermal matamorphism experienced by these mete-

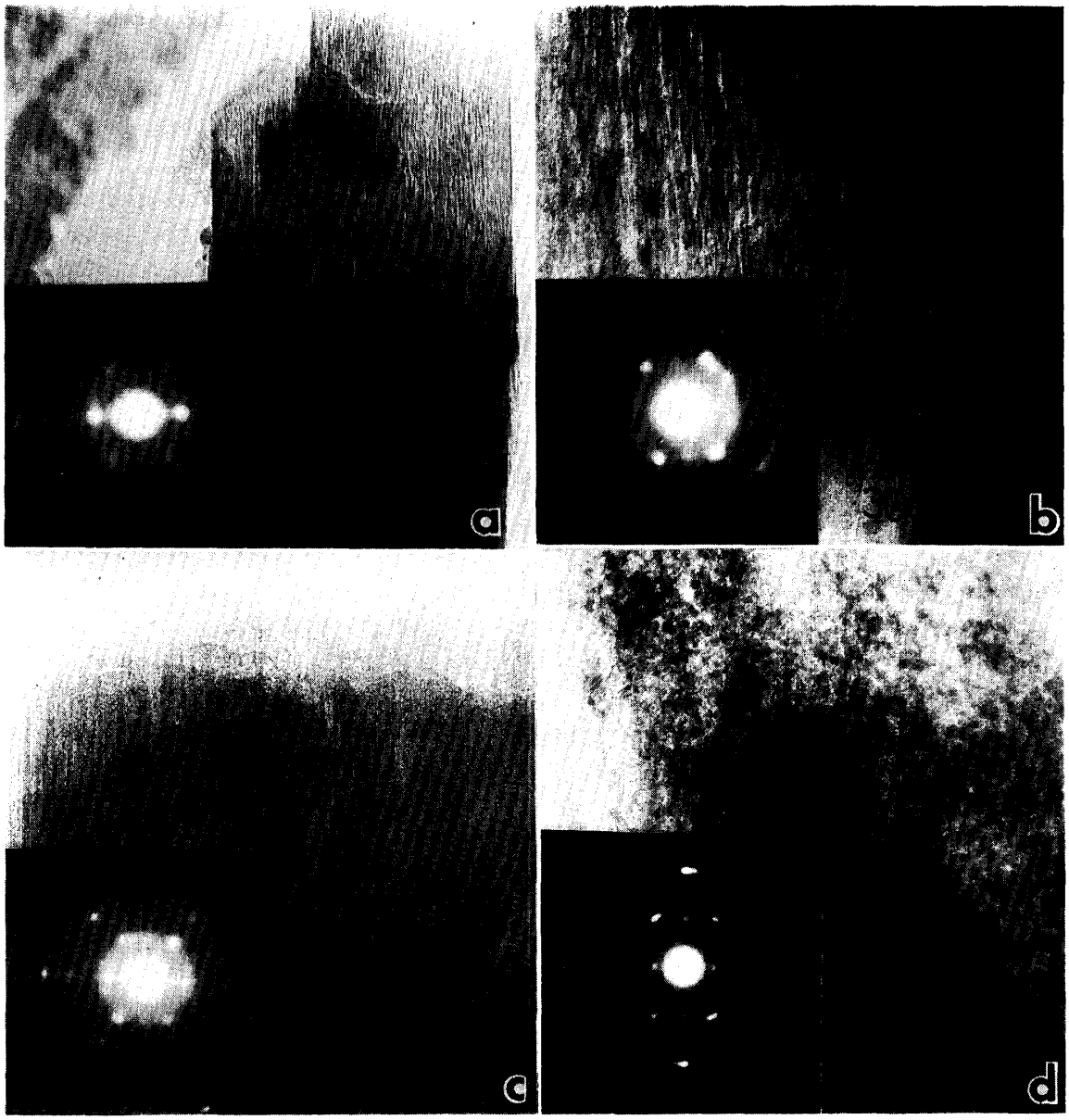

Fig. 9. EM images of serpentine in the Murchison CM chondrite heated for 48 hours in vacuo at, 400°C (a), 500°C (b) and 800°C (d). (c): Murchison Sample heated at 600°C in air for an hour.

orites, preliminary heating experiments of saponite and the Murchison CM chondrite were carried out. Iron-rich terrestrial saponite from the Green Tuff Formation (YOSHIMURA *et al.*, 1975) was used. The composition of this saponite (Table 1) is very similar to those of saponites in Y-86720 and Y-82162. The saponite samples were heated in air for an hour at 300, 400, 500, 600, 700, 800, 900 and 1000°C. Figure 8 shows TEM images of heated samples; thermal transformation occurred at above 900°C, and orthopyroxene and cristobalite were gradually formed. At temperatures below 800°C, sharp 9.5 Å diffraction spots corresponding to dehydrated saponite layers were recognized in both ED patterns. Small rounded materials which may have been newly crystallized are characteristic of the specimens heated at above 900°C. They

are similar to those observed in Y-86720 (Fig. 8). Thermal effects on Fe-saponite have not previously been examined in detail but some results of DTA and heating experiments are available (FAUST, 1951; SCHMIDT and HEYSTEK, 1953; MIDGLEY and GROSS, 1956). According to the previous workers, saponite generally shows a main dehydroxylation peak between 800°C and 900°C, and a subsequent exothermic peak is not clear in the DTA curve. However, the product obtained on firing saponite seemed to be enstatite, which appeared immediately after dehydroxylation (SCHMIDT and HEYSTEK, 1953). On the other hand, MIDGLEY and GROSS (1956) have reported the formation of enstatite and amorphous silica. Basal spacings of saponite before structural decomposition have been reported to be 9.7 Å at 500°C and 9.5 Å at above 600–750°C which corresponds to the inter-layer spacing of talc (MIDGLEY and GROSS, 1956). The present results are consistent with these previous ones.

Samples of saponite and Murchison were also heated *in vacuo* for 48 h. The results of heating saponite *in vacuo* for 48 h at 800°C were almost the same as those of heating saponite in air for 1 h at 800°C. However, in general, heating of phyllosilicates at some temperature *in vacuo* for a long time may correspond to heating at slightly higher temperature in air. For example, mineralogy and textures produced by heating of serpentine in Murchison *in vacuo* for 48 h at 400°C were similar to those of heating in air for an hour at 500–600°C (Fig. 9 and *cf.* AKAI, 1988). So, the temperature of thermal metamorphism estimated for Y-793321 by AKAI (1988) may be a little too high. Serpentine in Murchison which was heated *in vacuo* for 48 h at 800°C showed rather sharp olivine spots and diffraction halos disappeared. Heating samples in air for an hour may not be enough for completion of reaction. However, it may be reasonable, based on these heating experiments, to estimate only relative degrees of thermal metamorphism. Thus, it may be presumed as a first approximation that the phyllosilicates in Y-86720 and Y-82162 may have been heated at high temperatures, which correspond to heating at $\sim$800°C in air for an hour. On the other hand, PAUL and LIPSCHUTZ (1989) have estimated much lower temperatures based upon trace element analysis. This discrepancy needs to be clarified by further detailed heating experiments *in vacuo* for longer time. Y-793321 and B-7904 have also been reported to be thermally affected (AKAI, 1988). For temperature estimation of B-7904 more detailed examinations may be needed because its recently reported mineralogy suggests a complex mixture of saponite and serpentine (ZOLENSKY *et al.*, 1989b). However, it may have been heated probably at the highest temperature among these four specimens because no phyllosilicate structures were found and many irregularly shaped olivines were observed in B-7904 (AKAI, 1988). The present results suggest that Y-793321, Y-86720 and Y-82162 were thermally metamorphosed at relative degrees,

$$\text{Y-86720} > \text{Y-82162} > \text{Y-793321}\ .$$

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