

# The System Silica–Sodium Tetraborate

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The phase relations were established for the system silica–sodium tetraborate. The silica liquidus curve exhibits strong upward concavity but shows no flattening. The tridymite–cristobalite transformation occurred at  $1410^\circ \pm 10^\circ\text{C}$ . A lowering of the  $\alpha$  to  $\beta$  quartz inversion temperature of about  $9^\circ\text{C}$  was detected. Primary crystal habits are discussed. The region of metastable subliquidus immiscibility is also discussed and the nature of initial crystallization of the silica-rich liquid is shown.

## I. Introduction

THE system silica–sodium tetraborate includes the most technologically important region in the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ . The silica-rich area includes base compositions for many borosilicate glasses. Many Vycor-type glasses and partly devitrified ceramic-glass materials can be prepared from these compositions. In addition to ceramic and glass interests in this system, insight into several mineralogical problems, such as the crystallization of the silica minerals and the behavior of sodium borosilicate melts, can be obtained from a knowledge of the phase relations of this binary system.

## II. Literature Survey

The literature on individual compositions in the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  is voluminous. Only those studies pertinent to the delineation of the phase relations in the system  $\text{Na}_2\text{B}_4\text{O}_{13}-\text{SiO}_2$  are reported here. Hood and Nordberg<sup>1</sup> discussed the melting of several compositions in this binary system and described the separation of two amorphous phases at temperatures below that of the liquidus. Morey<sup>2</sup> presented a phase diagram for the system and reported a flattening of the liquidus between 50 and 70 wt% silica, but he observed no liquid immiscibility above the liquidus. Much work followed with emphasis on the nature of the immiscible phases. Work by Akimov presented the indices of refraction of the glasses in the system.<sup>3</sup> Electron microscopy on glasses in this system indicated to Vogel that three metastable liquid phases may coexist<sup>4</sup>: a silica-rich phase and two silica-poor phases, one of which is richer in soda than the other. Molchanova presented the range of compositions within the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  in which opalescent glasses can be prepared.<sup>5</sup> Ohlberg and Hammel, reporting on an electron microscope investigation of a glass lying within 1%  $\text{Na}_2\text{O}$  of the binary system, stated that the amorphous phases resulted from a subliquidus miscibility gap in the system.<sup>6</sup> Recently Cahn and Charles discussed the mechanism by which phase separation takes place in a glass from the binary mixtures.<sup>7</sup>

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The two end members of the system have been investigated thoroughly. Fenner established the phase relations in the system  $\text{SiO}_2$  in 1913.<sup>8</sup> The problem of the existence of tridymite as a stable phase of silica has been discussed by the present authors in another paper in which they concurred with Fenner's belief that tridymite is a stable phase of silica.<sup>9</sup> Sodium tetraborate was synthesized and described by Morey and Merwin.<sup>10</sup> Of the two forms of sodium tetraborate encountered by them, one appeared to be metastable and always transformed irreversibly to the normal  $\text{Na}_2\text{B}_4\text{O}_{13}$ . Only the stable phase was observed in this study. The sodium tetraborate referred to in the present paper is always the phase reported by Morey and Merwin as having the optical indices:  $\alpha = 1.499$ ,  $\beta = 1.252$ ,  $\gamma = 1.582$ .

## III. Procedure

The standard quenching technique was used.<sup>11</sup> Mixtures were prepared at 10 wt% intervals. The starting materials were  $\alpha$ -quartz (99.97%), supplied by the Malvern Minerals Company, and synthesized sodium tetraborate (99.983%).<sup>†</sup> After a tentative liquidus had been located, mixtures were melted, quenched to glass, crushed and remelted, and then held at  $100^\circ$  below the tentative liquidus permitting homogeneous nucleation. Firings were then made to determine the temperature at which the crystals were completely dissolved. The times required for equilibrium ranged from 10 min in the 10 $\text{SiO}_2$ :90 $\text{Na}_2\text{B}_4\text{O}_{13}$  composition to 200 hr in some of the more silica-rich compositions. Firing in sealed platinum capsules was used to make final liquidus determinations on the compositions with more than 70 wt% silica. Thus the expected volatilization of soda and boric oxide was prevented. Phases were identified by optical microscopy and X-ray diffraction. The inversion of quartz was checked using DTA and electron microscopy was used to investigate liquid immiscibility. Tem-Pres quenching furnaces were used and all temperatures were determined by Pt10Rh thermocouples calibrated against a standard supplied by The National Bureau of Standards. The furnaces were held to  $\pm 1^\circ\text{C}$  with controllers supplied with the furnaces.

## IV. Results and Discussion

The study included 246 firings on 12 compositions. No compound formation was encountered. Table I<sup>‡</sup> lists the firings pertinent to the delineation of the liquidus. Figure 1 shows the phase diagram and Table II gives the liquidus temperatures for the system. Unlike the curve presented by Morey the liquidus shows no flattening. The silica liquidus does, however, exhibit a major concavity upward expressing the strong departure from ideality of the liquids in the system. The sodium tetraborate liquidus is essentially a straight line.

Table III<sup>‡</sup> gives the data from which the eutectic was located. The eutectic temperature of  $724^\circ \pm 2^\circ\text{C}$  is higher by  $50^\circ\text{C}$  than that reported by Morey and the eutectic composition (34.5 wt% silica) is 2% richer in silica. In passing from the  $\text{Na}_2\text{B}_4\text{O}_{13}$  side of the eutectic to the silica side, crystallization rates change strikingly. Growth of quartz

<sup>†</sup> Analyses by Battelle Memorial Institute, Columbus, Ohio.

<sup>‡</sup> All omitted data (in Tables I and III) are available from the author.

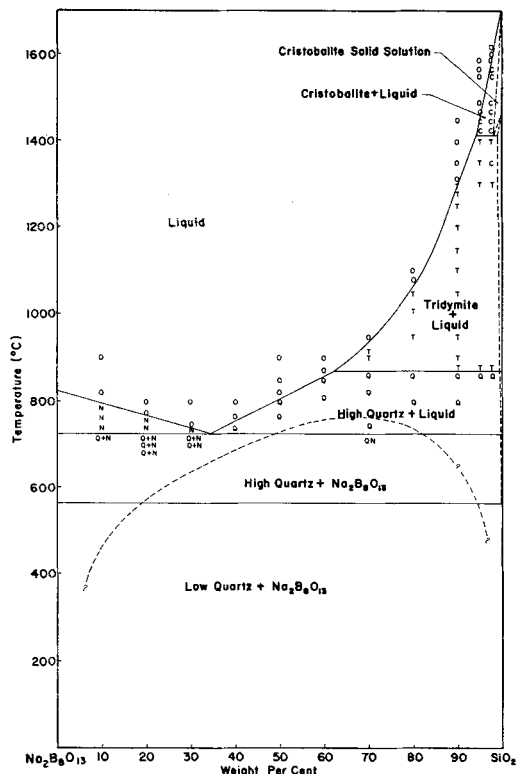


Fig. 1. Phase diagram for the system silica-sodium tetraborate. O = all glass, C = cristobalite and glass, T = tridymite and glass, Q = quartz and glass, N = sodium tetraborate and glass.

Table II. Liquidus Temperatures in the System Silica-Sodium Tetraborate

SiO <sub>2</sub> (%)	Na <sub>2</sub> O · 4B <sub>2</sub> O <sub>3</sub> (%)	Temp. (°C)
100.0		1710 ± 5
97.5	2.5	1590 ± 10
95.0	5.0	1462 ± 6
90.0	10.0	1303 ± 1
80.0	20.0	1065 ± 15
70.0	30.0	936 ± 16
60.0	40.0	860 ± 10
50.0	50.0	810 ± 10
40.0	60.0	747 ± 12
30.0	70.0	730 ± 5
20.0	80.0	763 ± 6
10.0	90.0	776 ± 8
	100.0	816 ± 0.5

crystals in the 40SiO<sub>2</sub>:60Na<sub>2</sub>B<sub>4</sub>O<sub>13</sub> composition requires 100 to 200 hr whereas sodium tetraborate will nucleate and grow in a matter of minutes in the 30SiO<sub>2</sub>:70Na<sub>2</sub>B<sub>4</sub>O<sub>13</sub> composition. Just below the eutectic temperature, however, growth of quartz in the sodium-tetraborate-rich compositions still takes 50 hr and below 600°C no devitrification of glasses was observed.

All the liquids can be quenched to glass. If any nuclei were present, however, in the 90% sodium tetraborate composition, only the fastest quenching could prevent dense crystallization of the melt. The indices of refraction of the glasses, given in Fig. 2, are in good agreement with Akimov's measurements for the ternary system.

The crystal habits of the primary phases are shown in Fig. 3. The initial cristobalite precipitated as angular dendritic-shaped crystals. Tridymite grew initially as acicular crystals which took on a lath-shaped twinned appearance with growth. High quartz grew doubly terminated hexagonal dipyramids; the sodium tetraborate occurred as euhedral lathlike crystals. An additional habit of cristobalite was

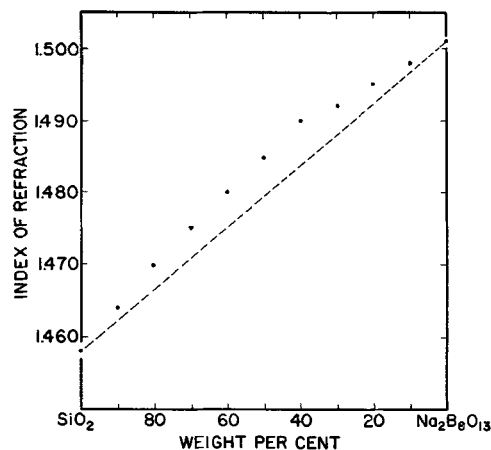


Fig. 2. Refractive indices of the glasses in the system silica-sodium tetraborate.

radiating needle-like crystals growing in a sphere. This habit was observed as a result of surface devitrification of silica-rich glasses and as a result of crystallization of the immiscible silica-rich glass phase. Crystallization of the silica-rich phase is discussed in the following section.

(1) Inversions of Silica

Tridymite was repeatedly encountered in various firings between the tridymite liquidus and composition 97.5% silica. The cristobalite-tridymite transformation occurred in this system at 1410° ± 10°C. In sealed capsules, all glass samples, tridymite and glass samples, and cristobalite and glass samples yielded tridymite after firing for 100 hr at 1400°C. The same starting materials yielded cristobalite and glass at 1420°C. The firings under the liquidus below 1400°C and above 870°C (with two exceptions) yielded tridymite crystals. Two 97.5SiO<sub>2</sub>:2.5Na<sub>2</sub>B<sub>4</sub>O<sub>13</sub> samples which were not sealed in platinum capsules gave cristobalite at 1325° and 1400°C. The texture of the fired samples was a friable mass. It is believed that Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> volatilized before the transformation could proceed. Without the sodium borosilicate liquid to act as a solvent for quartz and a transport agent for nucleation and growth of tridymite, the quartz grains were converted to cristobalite.

Kracek established the transformation temperature for tridymite to cristobalite in the system soda-silica at 1470° ± 10°C and this has been confirmed by many workers.<sup>12</sup> The 60° change in the transformation temperature, effected by the addition of B<sub>2</sub>O<sub>3</sub> to sodium-silica compositions, is suggestive of coupled solid solution of Na<sup>+</sup> and B<sup>3+</sup> in the cristobalite in accordance with the general formula, Na<sub>x</sub>B<sub>x</sub>Si<sub>2x</sub>O<sub>4</sub>, where x is the atomic fraction of boron substituting for silicon. No other evidence was encountered for the solid solution. No peak shifting could be observed in the diffraction patterns of cristobalite and although some change in the index of refraction should occur, it was not measured in this study.

No major effect was observed on the quartz-tridymite inversion. The highest temperature at which high quartz grew from the melts was 860°C. The lowest observed growth of tridymite was at 878°C. From the gap between these firings, it is obvious that some undetected change may exist in the reported quartz-tridymite inversion at 870°C.

The DTA was made on quartz crystals grown at 690°C for 570 hr in the 50SiO<sub>2</sub>:50Na<sub>2</sub>B<sub>4</sub>O<sub>13</sub> composition. This material began to invert to high quartz on heating between 563° and 564°C. On cooling the inversion began between 563° and 562°C. Using the same experimental design and the α-quartz used as a starting material in these studies, the inversion began at 572°C on heating and at 572°C on cooling, indicating a change of about 9°C in the high-low quartz inversion effected by solid solution.

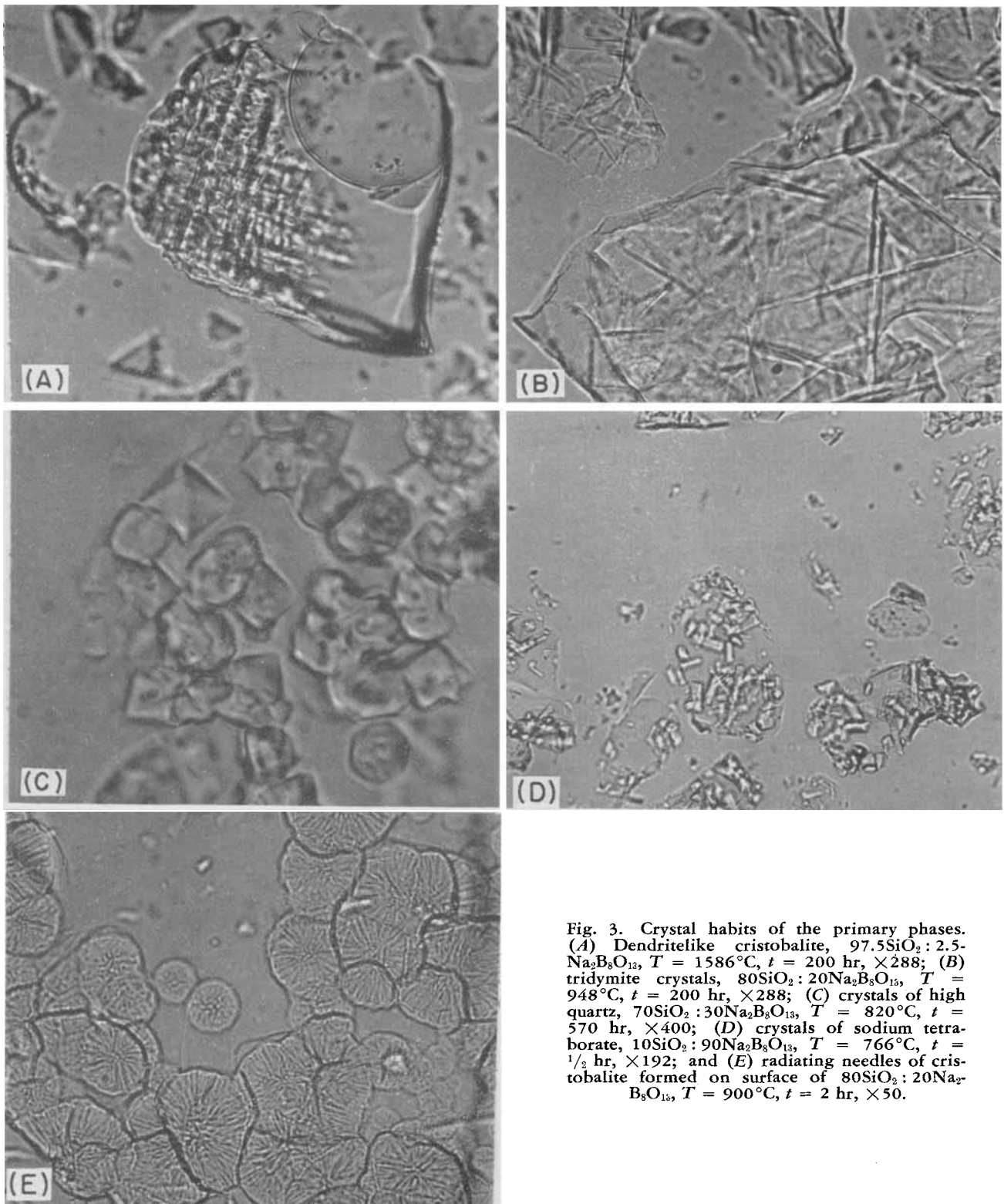


Fig. 3. Crystal habits of the primary phases. (A) Dendritelike cristobalite,  $97.5\text{SiO}_2:2.5\text{Na}_2\text{B}_8\text{O}_{13}$ ,  $T = 1586^\circ\text{C}$ ,  $t = 200$  hr,  $\times 288$ ; (B) tridymite crystals,  $80\text{SiO}_2:20\text{Na}_2\text{B}_8\text{O}_{15}$ ,  $T = 948^\circ\text{C}$ ,  $t = 200$  hr,  $\times 288$ ; (C) crystals of high quartz,  $70\text{SiO}_2:30\text{Na}_2\text{B}_8\text{O}_{13}$ ,  $T = 820^\circ\text{C}$ ,  $t = 570$  hr,  $\times 400$ ; (D) crystals of sodium tetraborate,  $10\text{SiO}_2:90\text{Na}_2\text{B}_8\text{O}_{13}$ ,  $T = 766^\circ\text{C}$ ,  $t = \frac{1}{2}$  hr,  $\times 192$ ; and (E) radiating needles of cristobalite formed on surface of  $80\text{SiO}_2:20\text{Na}_2\text{B}_8\text{O}_{13}$ ,  $T = 900^\circ\text{C}$ ,  $t = 2$  hr,  $\times 50$ .

## (2) Liquid Immiscibility

In a recent paper, Rockett *et al.* delineated the limits of the metastable subliquidus area of liquid immiscibility.<sup>18</sup> The area is shown by a dashed line in Fig. 1. The phase separation caused by this immiscibility is responsible for the opalescent appearance of glasses fired within the miscibility gap. The leaching of the soda-borate-rich phase leads to a silica-rich network glass which can be heat-treated to form high-silica glasses of the Vycor type. Figure 4 shows electron

micrographs of fractured surfaces of the  $50\text{SiO}_2:50\text{Na}_2\text{B}_8\text{O}_{13}$  glass which was heat-treated for 50 hr at  $603^\circ\text{C}$ . On heating this quenched glass (which shows the effects of spinodal decomposition) the silica-rich phase nucleates and grows in this composition as dendritelike structures. During replication of this 50% glass, a portion of a dendrite was pulled out of the glass and was embedded in the replica. The following electron diffraction pattern which was indexed as cristobalite was obtained from an octahedron formed in the silica-rich phase.

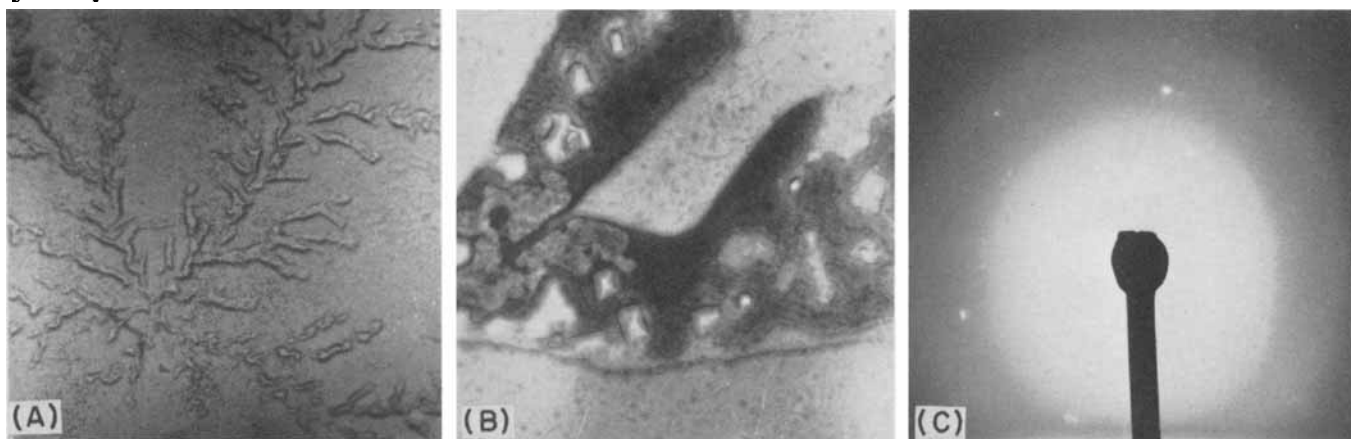


Fig. 4. Development of two phases in  $50\text{SiO}_2:50\text{Na}_2\text{B}_2\text{O}_7$  after 50 hr at  $603^\circ\text{C}$ . (A) Dendritic separation,  $\times 5400$ ; (B) dendrite leaf showing formation of cristobalite octahedra,  $\times 12,600$ ; and (C) diffraction pattern of cristobalite.

Electron diffraction $d(\text{Å})$	Cristobalite (ASTM card 4-0382) $d(\text{Å})$	$hkl$
2.81	2.84	102
2.00	2.02	202
1.69	1.60	203
1.40	1.40	223
1.26	1.28	322
0.940		

With prolonged heating at elevated temperatures, but still within the miscibility gap, the second phase spheroidizes and, having been nucleated with cristobalite crystals, they grow radially as the size of the sphere increases. The habit developed is identical to that shown in Fig. 3(E).

#### Acknowledgments

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# Phenomenological Theory of High Permittivity in Fine-Grained Barium Titanate

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The anomalously high permittivity in fine-grained ceramic barium titanate is explained by the absence of  $90^\circ$  twinning within the grains, giving rise to internal stresses as the ceramic cools below the Curie temperature. Using the Devonshire phenomenological thermodynamic method and a simplified model, the stresses involved are calculated. At these stress levels, the reduced strain calculated on this model agrees well with X-ray data for the fine-grained material. The limitations and possible developments of the proposed model are discussed.

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