

A new way of transformation from α -quartz to coesite*

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Abstract A laboratory method combining the high-energy mechanical ball milling and high static pressure has been suggested for modelling synthesis of coesite in the Earth's crust. A window of milling time, a mechanical collision-induced intermediate phase of α -quartz and its condition of easily crystallizing into coesite under the condition of 3.0 GPa, 923 K, < 1.0 min have been discovered. The new method needs much shorter synthesizing time and lower synthesizing critical pressure than those used before. The Raman spectra for the coesite synthesized by the present method have covered all the information of those natural and synthesized coesites reported before. It is demonstrated that this method has a great potential in geo-science research and implied the other possible mechanism of coesite formation in the Earth's crust.

Keywords: quartz-coesite, high-energy mechanical ball milling, high state pressure, Raman spectrum, metastable phase, subduction-exhumation of plate.

Based on the pressure and temperature^[1] of experimental transformation of α -SiO₂ to coesite under high static pressure (HSP), a conjecture has been made that the coesite in the Earth's crust (COSIEC) was formed during the process of a plate subducting into the upper-mantle (about 90 km), and then exhuming back to the Earth's surface. This hypothesis^[2-5] of plate subduction-exhumation has been put forward to explain the formation of the coesite^[6-11] existing in the Earth's crust in zones of building mountain of the Earth plates.

For 50 years, the study of COSIEC has been regarded as a "window" for knowing the Earth. In laboratories, much work^[12-15] on the synthesis of coesite by HSP and high temperature has been carried out, including the effect of the initial state of materials on the synthesis of coesite^[16-19]. However, it must be pointed out that for the hypothesis of plate subduction-exhumation, only the HSP condition after plates' subducting into the upper-mantle has been considered while the collisions between the plates before and during the subducting process have not. As is well known, the HSP does not reflect the factors of dynamic collision and shear stress, therefore, up to

now, there has been no suitable and direct method that can be used to test and verify the formation mechanism of coesite. Although the hypothesis of plate subduction-exhumation has been queried, it is still the only one explanation of the formation of COSIEC. Also, there are many differences between the pressure induced by dynamic collisions and HSP. In the former case, the pressure has both normal and shear stress; the pressure and temperature is obviously localized and inhomogeneous, and has a discontinuity in the role of time. In the latter case, the pressure is hydrostatic or quasi-hydrostatic; so it is mainly a normal stress with a more homogeneous and continuous role of time. The role of mechanical ball milling (MBM) has been studied by our group^[20-23]. We found that during the process of high-energy MBM, a high local pressure i. e. 3.0-6.0 GPa^[20-23] and temperature of 600-900 K or even higher (1750 K)^[21] could be generated by the impact of the steel balls. Also both a normal and shear stress could be produced by the high-speed collision of the steel balls with the three-dimensional vibration. Comparing the collision between the plates in the Earth and MBM, we found that there is a common localization of pressure (including normal and shear stress) and tempera-

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ture, but the difference exists in collision speed for the two kinds of collisions. Although the difference in space of the collisions between the plates in the Earth and MBM in the laboratory is significant, with the similarity, these two seemingly very different and unrelated collision phenomena can be related to each other. MBM can be used to study a modelling synthesis for the COSIEC according to the former common features, and can also be used to study the age-old collision dynamics of plates according to the latter difference through the high frequency collision of balls in the laboratory. Although the general MBM with low-energy is accustomed to be used in material science for pulverizing the starting materials, up to date, the effects of local dynamic pressure and shear stress on the synthesis of coesite have not yet been studied. Therefore, introducing high-energy MBM, which considers the factors of local dynamical mechanical collision and shear stress, and combining it with HSP as a research tool to study the transformation of α -SiO₂ to coesite for modelling the synthesis of COSIEC is a subject of considerable interest.

1 Initial material and experimental methods

The initial α -quartz powder has a purity of 99.0%, and its grain size is 505.8 nm accounting for 99.6% of grain distribution.

The initial α -quartz powder of 10 g, steel balls with diameters of 5–15 mm and weight of 150 g were placed into a stainless steel vial under an argon atmosphere, their mass ratio was 1:15. The rotating speed of ball milling vial was 750 r/min. A GN-2 type vibrating mechanical ball mill with a high-energy revolution was used for MBM. The milling vials rotated at a high speed in a planet-like arrangement in the vertical plane of mill and vibrated simultaneously at small amplitude in three dimensions. A small amount of samples was taken out every several hours for analysis.

A Rigaku D/max-r A 12 KW X-ray diffractometer (XRD) was used to record the XRD patterns with Cu-K_α radiation, and the least square method was used for determining the constants of crystal lattice in a scanning step of 0.02° and counting time of 0.4 s.

A belt-type two anvil press was used to study the crystallization of amorphous α -SiO₂ under HSP and high temperature^[24,25]. First, the MBM-treated α -SiO₂ powder was put into a boron nitride ampoule

which was encased into a graphite crucible, then pressed to a desired pressure and increased gradually to a required temperature, after being kept under high pressure and high temperature for expected time, the sample was quenched rapidly to room temperature at a cooling rate of about 10² K per second under high pressure. Finally, the pressure was released and the sample was obtained. For determination of pressure and temperature, see Ref. [26]. The pressure was calibrated by determining the relation between the press load and the phase transformation pressures of Bi, Tl, and Ba, and the temperature was detected by a Pt30% Rh-Pt6% Rh thermocouple. For the schematic of sample assembly, see Ref. [19].

The JY-HR 800 high-resolution Raman spectroscopy was used, $\lambda_{\text{ex}} = 632.8$ nm, wave number was corrected by the characterized peak 520 cm⁻¹ of single crystal Si, resolving power was 1 cm⁻¹.

2 Results and discussion

2.1 Pre-treating by mechanical ball milling

When studying the transformation of α -quartz (α -SiO₂) to coesite, the initial α -quartz powder was pre-treated by MBM. The process of amorphization of initial α -SiO₂ powder began at an MBM time of $t_{\text{mil}} = 10$ h; partial non-crystallization of the powder occurred at $t_{\text{mil}} = 15$ h, followed by a mainly non-crystallized state at $t_{\text{mil}} = 20$ h, and complete amorphization at $t_{\text{mil}} = 40$ h (Fig. 1).

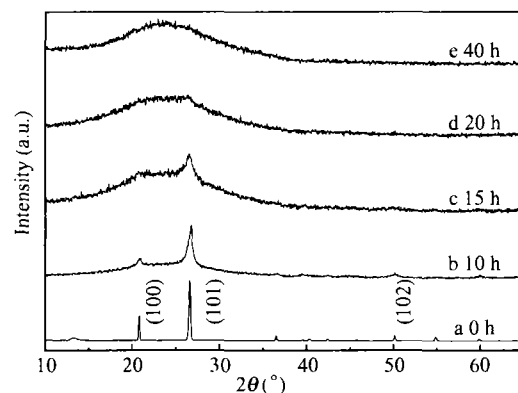


Fig. 1. The XRD patterns of initial α -quartz powder after being pre-treated by high-energy mechanical ball milling. a, XRD pattern of the initial α -quartz powder (hexagonal, $a = 0.4913$ nm, $c = 0.5405$ nm). b–e, the XRD patterns of initial α -quartz powder after being pre-treated by high energy MBM for $t_{\text{mil}} = 10$ h, 15 h, 20 h, 40 h, respectively.

XRD patterns of samples that have undergone

MBM from $t_{\text{mil}} = 60 \text{ h} - 250 \text{ h}$ are similar to those at 40 h, i. e. all in amorphous state; no MBM-induced crystallization appears. Increasing the rotating speed of MBM from 750 r/min to 800 r/min decreases the t_{mil} necessary for complete non-crystallization to 10 h. The condition for the onset amorphization of $\alpha\text{-SiO}_2$ induced by the collision of MBM is quite different from that by heating (1480 K, normal pressure) or HSP (9.8 GPa, 573 K), see Ref. [27].

2.2 High static pressure-induced crystallization of amorphous $\alpha\text{-SiO}_2$

MBM-treated $\alpha\text{-SiO}_2$ powder was used to study the crystallization of amorphous $\alpha\text{-SiO}_2$ under HSP and high temperature. From the XRD patterns (Fig. 2) of the pressure-induced crystallization products of amorphous $\alpha\text{-SiO}_2$, it was unexpected that there appeared coesite products induced by a HSP crystallization of amorphous $\alpha\text{-SiO}_2$ just within a limited and definite range of t_{mil} , but no coesite products produced for longer t_{mil} beyond the range, i. e. there existed a "window" of milling time: $10 \text{ h} < t_{\text{mil}} < 40 \text{ h}$. For $\alpha\text{-quartz}$ at $t_{\text{mil}} = 0 \text{ h}$, its structure did not change after the application of HSP (4.0 GPa, 923 K, 30 min). For $t_{\text{mil}} = 15 \text{ h}$, there occurred a single phase of coesite; for $t_{\text{mil}} = 25 \text{ h}$, mainly coesite; for $t_{\text{mil}} = 35 \text{ h}$, coesite and $\alpha\text{-quartz}$ co-existed; for $t_{\text{mil}} = 40 \text{ h}$, $\alpha\text{-quartz}$ accompanying with a small amount of FeSiO_3 impurity. The grain size distribution for the MBM-treated $\alpha\text{-quartz}$ powder has been detected by a laser analyzer of grain size. The grain sizes and their proportions for the $t_{\text{mil}} = 0 \text{ h}$ are 505.8 nm, 99.6% and 2408.5 nm, 0.2%, respectively. For the $t_{\text{mil}} = 15 \text{ h}$, are 486.5 nm, 48.3%; 763.8 nm, 50.4%; and 1060.3 nm, 1.2%, respectively. For the $t_{\text{mil}} = 25 \text{ h}$, are 343.4 nm, 96.8% and 1576.5 nm, 3.2%, respectively. For the $t_{\text{mil}} = 35 \text{ h}$, are 461.3 nm, 91.8% and 216.2 nm, 8.2%, respectively. For the $t_{\text{mil}} = 40 \text{ h}$, are 529.6 nm, 81.7% and 229.6 nm, 18.3%, respectively. The data show that the laser analyzer of grain size can be used to measure the granular size well. The measuring precision of crystal grain size could be disturbed by the aggregation of grains. With increasing the milling time, grains are fining and turned into amorphous state partially at first, then growing in size appropriately and being accompanied with amorphization completely; and there appears a minimum in the relation between the size of small grain with a larger proportion pulverized by

MBM and the milling time, which agrees qualitatively with that measured from X-ray small angle scattering. In addition, the relations between the grain size with t_{mil} and the coesite products with t_{mil} , for example, the $(1-x)/x_{\text{max}}$ with t_{mil} , where the x is the content of coesite, are apparently similar to each other, however, the inherent link has not yet been found for the grain size of MBM-treated powder and the coesite products of crystallization.

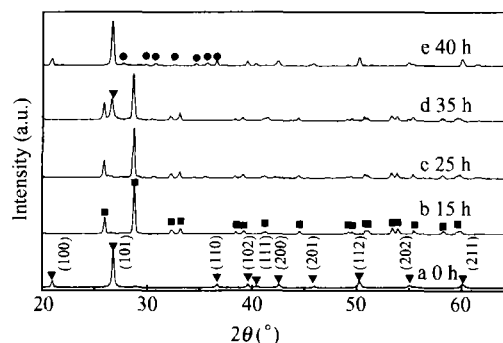


Fig. 2. The XRD patterns of high static pressure products synthesized under 4.0 GPa, 923 K, 30 min for initial $\alpha\text{-quartz}$ powder pre-treated at different t_{mil} . ∇ - $\alpha\text{-SiO}_2$; \blacksquare -Coesite; \bullet - FeSiO_3 .

2.3 Mechanical collision-induced metastable phase of $\alpha\text{-quartz}$

Since Raman spectroscopy can be used to "fingerprint" crystalline structures^[28-31], this method has been used to study the above-mentioned MBM-treated $\alpha\text{-quartz}$ amorphous powder. From the Raman spectra (Fig. 3), it can be seen that during the process of MBM-induced amorphization for the $\alpha\text{-quartz}$ powder, an intermediate metastable phase appears, which is characterized by the 484 cm^{-1} , 603 cm^{-1} , and 962 cm^{-1} Raman peaks within the range $t_{\text{mil}} = 0 - 40 \text{ h}$. When $t_{\text{mil}} = 15 \text{ h}$, the spectrum of metastable phase is the most intense, then gradually weakens as t_{mil} increases, and finally disappears at $t_{\text{mil}} = 40 \text{ h}$. From the process of formation and disappearing, it is very easy to understand the phenomenon shown in Figs. 3 and 4 that coesite exists only within the range $t_{\text{mil}} = 15 - 35 \text{ h}$; no coesite exists at $t_{\text{mil}} = 0 \text{ h}$ and 40 h . The appearance of an intermediate phase of $\alpha\text{-quartz}$ during the process of high-energy MBM is the prerequisite condition for producing coesite by high-pressure induced crystallization of amorphous $\alpha\text{-quartz}$. If the $\alpha\text{-quartz}$ powder is subjected to low energy MBM, the intermediate phase does not appear, and therefore no coesite appears even if it is treated under the same HSP condi-

tion of 4.0 GPa, 923 K, 30 min as treated as before.

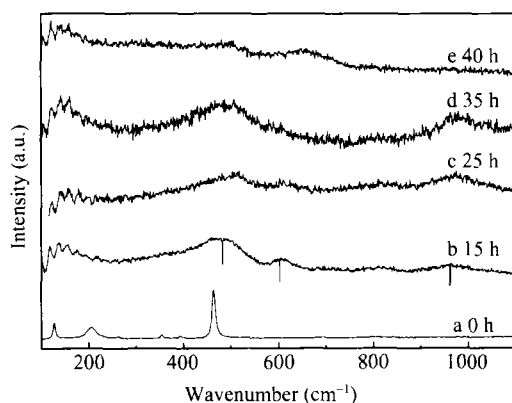


Fig. 3. The Raman spectra of amorphous α -quartz powder for initial α -quartz powder pretreated at different t_{mil} . For the amorphous α -quartz powder of $t_{\text{mil}} = 15$ h, there appears an intermediate metastable phase of α -quartz, which indicated by bars in the Figure.

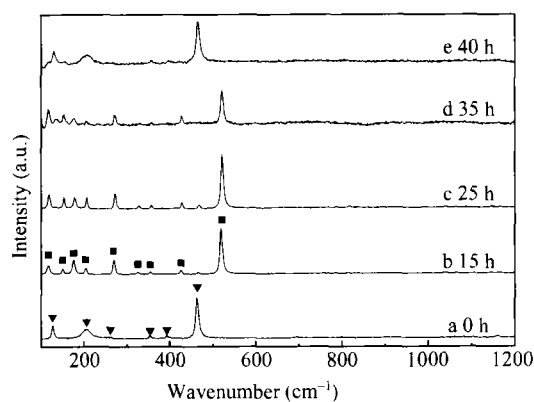


Fig. 4. The Raman spectra of high static pressure-induced crystallization products of amorphous α -quartz. The conditions of t_{mil} and high-pressure synthesis are shown as in Fig. 2. \blacktriangledown - α -SiO₂; \blacksquare -Coesite.

It should be noted that the intermediate metastable phase of α -quartz, which occurred in the process from crystalline to amorphous state of α -quartz induced by MBM, is very sensitive to the details of MBM condition and the initial state of α -quartz, so to further study the regularity of formation for the metastable phase of α -quartz is very important. In addition, high static pressure induced coesite could appear for those α -quartz powder pre-treated by high-energy MBM within the range of t_{mil} from 40 h to 250 h, if the synthesizing condition exceeds 4.0 GPa, 923 K, 30 min. Also, there seems existing still an interesting problem needed to be investigated here, that is, maybe one could not exclude a possibility of

existing another window of milling time within the range of t_{mil} from 40 h to 250 h. In light of the feature transforming gradually into amorphous for α -quartz by MBM, intermediate metastable phase of α -quartz can be produced for the other grain sizes. It is worthy to study carefully whether there appear multiple-windows of milling time ranging from 40 h to 250 h or not, despite that no coesite was observed at only a few t_{mil} within the range in our study.

The results of assigning the Raman spectra of Fig. 4 are listed in Table 1. The Raman spectrum of the coesite synthesized by the present method, that of the natural COSIEC which has been discovered, and that of the coesite synthesized by Mirwald^[12] are compared in Table 2. It is interesting that the data of Raman peaks for the coesite synthesized by the present method have covered over those of both the natural and synthesized coesites. The number of Raman peaks for the present paper is one more than that of the natural coesites found in Italy^[6], Norway^[7], and is the same as the samples from China^[9,10] and South Africa^[8]. There are, however, five additional peaks not found in the spectra of the coesite synthesized by Mirwald^[12]. Up to this point, we obtain a Raman spectrum of synthetic coesite with the biggest number of peaks. Correspondingly, from the crossed polarized micrographs, it is seen that the micrograph of the coesite used in this work is very similar to that of natural coesite. These demonstrate that although the differences in space and speed of the collisions between the plates in the Earth and the MBM in laboratory are very great, and also all the specific ways of collision are not the same, the Raman spectra we recorded are much better than those previous ones obtained only by HSP without considering the factors of local dynamic pressure and shear stress, and more precisely reflecting the nature of natural COSIEC, because the above-mentioned factors reflecting their similar essence of the two collision phenomena have been considered. At the same time, it is also demonstrated that pre-treating α -quartz initial powder by high-energy MBM is a simple, physical and efficient method for the laboratory synthesis of coesite that closely resembles that found in the Earth's crust. The efficient method of modelling synthesizing the natural coesite in the laboratory is of great importance to the researching on the formation mechanism of COSIEC because of its certainly not duplicating the complicated formation histories of natural coesite in the Earth's crust.

Table 1. The peak positions (cm^{-1}) and their assignments of Raman spectra for pressure-induced crystallization products of amorphous α -quartz

α -quartz	15 h	25 h	35 h	40 h	Assignment	VM
	117	119	117		CS	B_g
127				129	QZ	E
	151	152	152		CS	A_g
	177	178	177		CS	B_g
206	205	206	205	206	CS+QZ	$A_1 + E$
263				266	QZ	E
	270	271	270		CS	B_g
	326	326	329		CS	$A_g + B_g$
356	356	356	356	358	CS+QZ	$A_g + A_1$
394				396	QZ	E
	426	428	427		CS	B_g
463	467	467		465	QZ	A_1
	520	522	522		CS	B_g

The conditions are shown as in Fig 2. CS, coesite; QZ, α -SiO₂; VM, Raman vibration mode, A_g , B_g , A_1 , E, see Ref. [28–31].

Table 2. Comparison of Raman peak positions (cm^{-1}) for coesite synthesized in this study to that of natural coesite and synthesized by Mirwald^[12]

Intensity	Natural coesite				Synthetic coesite	
	Italy	Norway	China	S. A.	Mirwald	Present work
S	118	118	118	117	117	117
M	151	150	151	151	—	151
S	177	177	177	177	177	177
M	205	204	205	205	—	205
S	271	270	271	271	270	270
W	—	326	326	326	—	326
M	356	355	356	356	—	356
M	427	—	426	425	—	426
	466	466	466	466	465	467
S	521	521	521	521	520	520

S, strong; M, middle; W, weak; S.A., South Africa. The Raman peak positions for the synthesized coesite by Mirwald and the natural coesite found in Italy^[6], Norway^[7], and South Africa^[8] are given in Ref. [28]; China^[10] in Ref. [29].

2.4 Coesite and its implications

The above-mentioned results are typical for the HSP synthesis of coesite under the condition of 4.0 GPa, 923 K, 30 min. The effects of HSP and time on the products of synthesis have been studied carefully. Using the amorphous α -quartz of $t_{\text{mil}} = 15$ h with metastable phase, under 923 K and 60 min, the study of HSP synthesis indicates that coesite of a single phase, or nearly single phase, can be obtained as long as the pressure is at least 3.0 GPa^[32]. This represents the critical pressure for synthesizing coesite, below which coesite does not form. Under the condition of 3.0 GPa, 923 K with a synthesis time between 1 min and 60 min, the crystallization products of amorphous α -quartz powder are a pure form of

monoclinic coesite ($a = 0.717$ nm, $b = 1.238$ nm, $c = 0.717$ nm, $\beta = 120^\circ$; see Fig. 5). Therefore, after pre-treatment by high-energy MBM, the synthesizing conditions for coesite (3.0 GPa, 923 K, 1 min) are much lower than the conventional ones (3.5–6.0 GPa, 773–1473 K, 2–48 h), especially there exists a great difference in synthesizing time. This can be ascribed to the local high pressure (3.0–6.0 GPa), and local high temperature (600–900 K or even higher), introduced by the shear and normal stresses resulting from high-energy MBM collisions, and to the appearance of intermediate metastable phase of α -quartz. The condition, 3.0 GPa, 923 K, 1 min, of easily synthesizing the coesite is also an important finding obtained in our experiment.

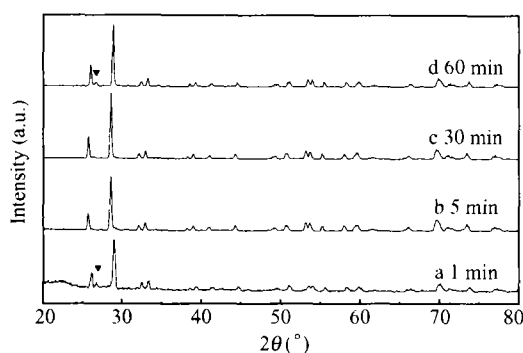


Fig. 5. The XRD patterns of products synthesized under 3.0 GPa, 923 K, and different times of maintaining pressure and temperature. The times of maintaining pressure and temperature were 1 min a, 5 min b, 30 min c, 60 min d. The initial α -SiO₂ powder was pre-treated with $t_{\text{ml}} = 15$ h. ▼- α -SiO₂.

As well known, there are two hypotheses of subduction-exhumation of plate, one is of the deep-subduction, the majority; the other is of the shallow-subduction, the minority. The critical synthesizing pressure of coesite, 3.0 GPa, obtained in this study is lower than that 3.5 GPa reported by Coes^[1], which implicates that the subduction depth of plate would be of about 20 km shallower than the common accepted value, and the mechanism of shallow-subduction is also a possible one, if the factors of local collision and shear stress have been considered.

It is surprising that for amorphous α -quartz powder of the $t_{\text{ml}} = 15$ h, under 3.0 GPa and 923 K, considerable coesite products (over 50% of the sample.)^[32] can be obtained when the time of maintaining pressure and temperature is shorter than 1 min, even it needs not any time of maintaining pressure and temperature as long as the sample has been undergone an increasing pressure and temperature up to 3.0 GPa and 923 K. So, when the factors of local dynamic pressure and shear stress are considered and pre-treatment of high-energy MBM has been adopted, the HSP synthesizing condition for coesite, 3.0 GPa, 923 K, and < 1 min (about ten seconds), transforms into a mode of "high-speed" synthesis. This synthesizing time is much shorter than that of 15 h reported by Coes,^[1] however, it is much longer than that from meteorite collision (ms), explosive shock-wave (μ s), and laser shock-loaded impact (ns). Therefore, after considering the local dynamical pressure and shear stress, and introducing the pre-treatment of high-energy MBM, the synthesizing condition of coesite would change from a low-speed to a high-speed mode and consequently from a "HSP metamorphic role" to a "impact metamorphic role"

mode. The phenomenon of "high-speed" synthesis mode of coesite induced by the present method may give an implication for geo-science here that in the Earth's crust in zones of building mountain for the Earth plates, an intermediate phase of α -quartz can be created in the place where underwent collisions between the plates, and could then form coesite after being interacted instantaneously with a strong earthquake wave and/or stress (pressure ≥ 3.0 GPa, and temperature ≈ 923 K) coming from the Earth, or meet with a more appropriate collision of plates. In fact, there would be some local non-stable system existing in the Earth's crust, induced by stress surrounding the system and so on. When the system is subjected to an instantaneous interaction or disturbance coming from the Earth, even if it is a weak earthquake wave and/or other weak stress (pressure $\ll 3.0$ GPa, and temperature ≈ 923 K), from the physical point of view, the system might loss its stability due to the flip-flop, and consequently is accompanied simultaneously with occurring of a new earthquake wave and some changes including the local transformation from quartz to coesite. Therefore, by the introduction of local pressure and local temperature and shear stress, the synthesizing time of coesite has been shortened greatly, which has predicted a possible new formation mechanism of coesite, that is, coesite can be produced in the place where exists a local non-stable system in the Earth's crust after its being interacted with an earthquake wave and/or stress.

There is a term of "mylonitization" in geology, it means a dynamical metamorphic process of fining the rock by shear stress. Recently a research shows that the shear stress appears in a special environment including rheology and re-crystallization, etc. The malleable shear zone would be formed in any zone of building mountain of the Earth plates, and the mylonitization might occur in the malleable shear zones, consequently, the mylonitization makes the minerals fining and amorphization. It is very similar to the fining and amorphization process of pre-treating quartz by high-energy MBM. Now that the shear zone in the Earth's crust might create the mylonitization of rock (quartz), and result in fining and amorphization, when the metastable phase of amorphous quartz is subjected to an earthquake wave generated from the Earth, the coesite would take place directly in the Earth's crust and needs not the undergoing of subducting into the upper-mantle (about 90 km). Thus, here appears a new possible formation mechanism of

coesite.

3 Conclusions

Considering the similarity between the local collisions between the Earth's plates and the collisions in high-energy MBM, we have adopted the pre-treatment of α -quartz powder by high-energy MBM, and suggested a laboratory method for modelling the synthesis of COSIEC. A window of milling time, a new intermediate phase of α -quartz characterized by the Raman peaks of 484 cm^{-1} , 603 cm^{-1} , and 962 cm^{-1} , and a Raman spectrum of synthetic coesite with the biggest number of peaks up to now obtained by the present method have been discovered. The intermediate phase, which resulted from the local high-pressure and high-temperature, and shear stress generated by collisions with steel balls, is the reason in structure why the coesite is easy to be synthesized under the condition of 3.0 GPa , 923 K and $<1\text{ min}$. The discovery of the phenomenon of high-speed synthesis (about tens of seconds) of coesite is important. The possible transformation from α -quartz to coesite occurs in the place where the intermediate phase of α -quartz presents during the collision process of the Earth's plates. After the formation of the metastable phase, the final transformation of α -quartz to coesite needs the conditions of high-pressure induced by a shock wave from earthquake wave and/or stress coming from the Earth, or by further available plate collisions. The discovery of intermediate metastable phase of α -quartz during its process of crystalline-amorphization transformation in this paper could shed a new light on the metastable paths by which coesite might be formed in the Earth's crust. The fact that the COSIEC exists is simply a prerequisite for proving the tenability of the hypothesis of subduction-exhumation of plate, not its sufficient condition. We argue that there exists another possible formation mechanism for COSIEC and show that the study on modelling synthesis of COSIEC can be used to trace back to the age-old collision dynamics process of plates and to find the records of some earthquakes and other information.

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