

Review Article

Progresses in Fluid Inclusion Synthesis in Quartz

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High-temperature and high-pressure (HTHP) fluids are one of the most extensive participants in geological events. The representative in situ sampling of the HTHP fluids, which is an essential prerequisite for precisely characterizing the HTHP fluids (including compositional and volumetric properties), has been a vital challenge. The technique of fluid inclusion synthesis (FIS) in quartz is one of the only options. It has experienced an almost 40-year development since the standard fracture healing method was invented. Considerable advances in our understanding of physicochemical properties of geological fluids and their roles in many geological processes have been achieved by the use of the FIS techniques. A set of methodologies for fluid inclusion synthesis have been established. Great progresses have also been made, which includes the various pretreatment FIS techniques, the in situ fracturing FIS technique closely associated with the HTHP apparatus, the in situ fracturing refilled FIS technique for large fluid inclusion synthesis at controlled time under unfavorable conditions, and the novel fluid inclusion synthesis by fused silica capillary. Such great many progresses of the quartz FIS techniques have been scattered in the geochemists' individual research work, and systematic collection and objective evaluation are missing. Consequently, we synthesize existing research, describe and identify the basic operations, discuss the methodological issues like pros and cons, and highlight the problems and prospects of the quartz FIS techniques. Furthermore, it is suggested that in situ and (or) large volume fluid inclusion synthesis will be an important future direction in view of the growing applications of the FIS techniques in combination with microanalytical techniques, especially the Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Our review would provide technical guidance to those who wish to investigate HTHP fluids and be beneficial to the future development and applications of the FIS techniques.

1. Introduction

Originated from the researches to the natural fluid inclusions, the techniques of fluid inclusion synthesis (FIS) have been developed largely on the basis of the great achievements in fluid inclusion studies and experimental geochemistry. The FIS technique utilises the fact that hydrothermal recrystallisation and healing of fluid-filled fractures in minerals are generally imperfect such that samples of the ambient fluid become isolated as inclusions along the annealing fracture and crystal growth surfaces. As with natural fluid inclusions, the synthesized inclusions represent in situ microscopic samples of the fluid entrapped in the course of high-temperature and high-pressure (HTHP) experiments,

at least to a first approximation. The advantage of the synthetic fluid inclusions is that they remain closed systems on quenching such that the bulk compositional and volumetric properties of the HTHP fluids are preserved and hence may be determined using ex situ analytical methods. So it is by the use of FIS techniques that considerable advances in our understanding of physicochemical properties of geological fluids and their roles in many geological processes have been achieved (e.g., [1–7]).

Fluid inclusion synthesis was originally identified by Sorby [8] in salt, which is the first example of synthetic primary fluid inclusions, while the first examples of synthetic secondary fluid inclusions (crack healing) are from Laemmlein [9] and Lemmlein [10] in NaNO_3 . The fluid inclusion

synthesis in synthetic quartz was firstly reported by Roedder and Kopp [11]. To figure out the effect of pressure correction on inclusion thermometers, the researcher synthesized primary fluid inclusions in quartz crystals within sealed vertical autoclaves under known temperature, pressure, and fluid composition. Subsequently, Shelton and Orville [12] proposed the original fracture healing procedures to synthesize fluid inclusion within mechanically fractured natural quartz. Given the low efficiency of the mechanical fracturing, a standard FIS technique which incorporated a simple and effective thermal shock prefracturing procedure was invented by Sterner and Bodnar [1]. The standard FIS technique “opened a window” in fluid inclusion studies and experimental geochemistry and was successively applied to a series of studies, such as formation mechanism and postentrapment modifications of fluid inclusions (e.g., [1, 3, 13–38]); phase equilibrium properties and PVT or PVTX relations of a variety of chemical systems (e.g., [39–49]); solubility, speciation, mobility, and partitioning of selected elements (e.g., [4, 6, 24, 50–71]); and origin and reaction of oil or natural gas [72–74].

Over the past decades, the quartz FIS techniques have been developed rapidly, including not only additional pretreatment FIS techniques but also improvements of the in situ fracturing FIS techniques with growing popularity. Moreover, to meet special requirements, some researchers created an in situ fracturing refilled FIS technique, and other scientists also established a novel way to synthesize fluid inclusion by fused silica capillary. In conclusion, the quartz FIS techniques have been becoming more mature and applied in many fields of Earth Science, such as the calibration of relevant instruments for fluid inclusion analysis (e.g., [32, 75–78]) and experimental investigations involving conditions close to the lower crust, upper mantle, and subduction zones (e.g., [7, 50, 62, 65, 79]). However, many progresses of the quartz FIS techniques have been scattered in geochemists’ individual research work unfortunately and systematic collection and objective evaluation have been missing for long. Consequently, in our contribution, the latest progresses of the quartz FIS techniques are collected and reviewed, which should be beneficial to the future developments and applications of the FIS techniques.

2. FIS Techniques

In principle, the FIS technique is mostly based on producing significant microfractures in the host mineral (quartz) and then healing as well as possible in the sealed capsule in a HTHP cavity. With this procedure, the coexisting HTHP fluid will be captured by the host mineral (quartz) to form fluid inclusions (Figure 1). Mainly based on the appearance of the microfractures and related fluid inclusions in the host minerals in different times, the FIS techniques can be roughly divided into two categories, namely, the pretreatment FIS techniques (or the ex situ fracturing FIS techniques) and the in situ fracturing FIS techniques. The former commonly requires the host mineral (quartz) to be pretreated to produce fissures (pits or channels) before being subjected to high-temperature and high-pressure cavities,

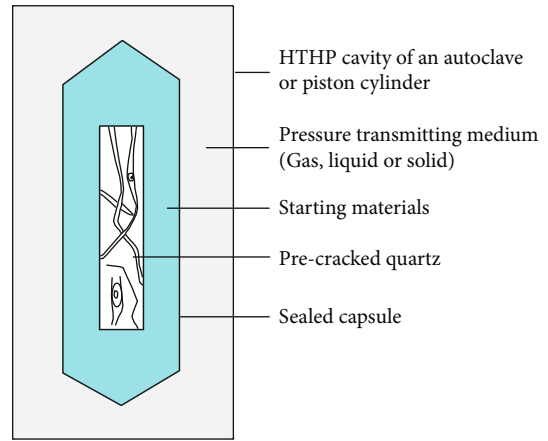


FIGURE 1: Sketch of the fluid inclusion synthesis within high-temperature and high-pressure equipment (not proportionate).

while the latter has the host mineral (quartz) fractured inside the high-temperature and high-pressure cell at a certain time during the experiment. In the pretreatment FIS techniques, the pretreatment procedure is quite critical, while the following procedures (such as starting material loading, capsule configuration and sealing, sample assemblies, and temperature and pressure routing) are roughly the same. Depending on high-temperature and high pressure equipment, the in situ fracturing FIS techniques are more complicated and will be introduced in detail in Section 2.2.

The overall situation of fluid inclusion synthesis in quartz has been compiled and shown in Tables 1–5, including parameters like specific FIS technique, temperature and pressure, durations, experimental apparatus, inclusion size, and applications. The high-temperature and high-pressure apparatus used for FIS mainly comprise the cold-seal pressure vessels, the rapid-quench autoclave/pressure vessels, and the piston cylinder. Adopting gas or pure water as pressure transmission medium, the first two devices own relatively large pressure cavities but are generally used under pressures lower than 1 GPa. The latter was invented by Boyd and England [80], with the capability of reaching pressure values of 5 GPa and the temperature of 1600°C.

2.1. The Pretreatment FIS Techniques

2.1.1. Prefracturing FIS Technique. The traditional fracture healing FIS technique includes a critical thermal shock prefracturing procedure. The usual practice is that quartz prisms (cores or chips) cut from inclusion-free quartz crystals are heated up to a certain temperature and then quenched in cold distilled water immediately upon removal from the oven. The temperature is usually between 300°C and 550°C (Table 1; optimum at 350°C) with pressure at ambient conditions, which is plotted in the stability field of α -quartz. Following the procedure, a large number of cracks are generally produced in the quartz. Thereafter, fluid inclusions would form along the fractures during the later fracture healing. It is worth mentioning that Zajacz et al. [69] selected a higher temperature (700°C) within the procedure

TABLE 1: Some typical applications of the prefracturing FIS techniques with thermal shock procedure.

Number	Thermal shock temperature	T (°C)	P (MPa)	Run time (h)	High-temperature and high-pressure apparatus	Inclusion size	Applications	Literatures
1	350°C	200~850	50~700	3~2088	Pressure vessels	/	Studies on synthetic fluid inclusions	[1]
2	350°C	550~1000	50~130	48~480	Cold-seal pressure vessels	5~50 μm	Determination of phase equilibrium properties	[40]
3	350°C	350~700	200~400	120~1008	Cold-seal pressure vessels	10~20 μm	Experimental determination of PVT properties	[49]
4	350°C	350~650	50~100	120~336	Rapid-quench autoclave	10~50 μm	Studies on synthetic fluid inclusions	[32]
5	350°C	700	100	168	Rapid-quench autoclave	5~20 μm	Synthetic fluid inclusion of $\text{CaCl}_2\text{-H}_2\text{O}$ system	[22]
6	350°C	524~725	310~1700	137~454	Piston cylinder	10~50 μm	Copper solubility in hydrothermal brines	[57]
7	350°C	600~750	2200	120~452	Piston cylinder	5~100 μm	Element mobility from subducted sediments under conditions in subduction zones	[62]
8	350°C	120~350	50	480	Rapid-quench autoclave	10~20 μm	Experimental study on synthetic oil-bearing inclusions	[33]
9	300~320°C	500~800	200	552~840	Cold-seal pressure vessels	$n \sim n \times 10 \mu\text{m}$	Experimental study of the NaF-bearing fluids	[31]
10	300~320°C	350~440	100	35~90	Autoclave	$n \sim n \times 10 \mu\text{m}$	Experimental study of the water-sodium sulfate system	[29]
11	700°C	1000	150	48	Rapid-quench (TZM) vessels	10~50 μm	Alkali metals control the release of gold from volatile-rich magmas	[69]
12	350°C	300~700	100~500	120~960	Cold-seal pressure vessels	$\geq 5 \mu\text{m}$	Experimental determination of the PVTX properties of $\text{H}_2\text{O-CH}_4$	[48]
13 ^c	/	800	710~2610	24~94.5	Piston cylinder	$\geq 150\text{-}200 \mu\text{m}$	The mobility of U and Th in subduction zone fluids	[50]
14	350~375°C	800	100	168	Rapid-quench autoclave	5~20 μm	Experimental study on synthetic fluid inclusions of $\text{NaCl-H}_2\text{O-CO}_2$ system	[27]
15	/	725~850	1500~2600	24	Piston cylinder	5~20 μm	Immiscibility between water and hydrogen in earth's mantle	[7]
16	400°C	300~600	337	456	Cold-seal autoclave	10~30 μm	Fluid inclusion modification by H_2O and D_2O diffusion	[24]
17	/	700~800	2500~2600	44~117	Piston cylinder	10~50 μm	Fluid-rock equilibria at the slab-mantle interface	[79]
18	350°C	600~800	50~100	96~336	Cold-seal pressure vessels	10~30 μm	Partitioning of Na and K between liquid and vapor in the $\text{H}_2\text{O-NaCl-KCl}$ system	[64]

TABLE 2: Some typical applications of the preablating FIS technique.

Number	T (°C)	P (MPa) _a	Run time (h)	High-temperature and high-pressure apparatus	Inclusion size	Applications	Literatures
1	550~725	110~400	552~840	Cold-seal vessels	$\geq 75 \times 500 \mu\text{m}$	Gold solubility in supercritical hydrothermal brines	[4]
2	300	10	720	Autoclave	$< 15 \mu\text{m}$	Production of synthetic fluid inclusions in the $\text{H}_2\text{O-CH}_4\text{-NaCl}$ system	[81]

TABLE 3: Some typical applications of the preetching FIS technique.

Number	Acid or alkali	T (°C)	P (MPa)	Run time (h)	High- temperature and high- pressure apparatus	Inclusion size	Applications	Literatures
1	/	750	700	115~168	Piston cylinder	2~60 μm	Validation of LA-ICP-MS fluid inclusion analysis	[75]
2	HF	700	200	72	Rapid-quench autoclave	20~40 μm , max 100 μm	Synthesize large fluid inclusions in quartz at controlled times and under unfavorable growth conditions	[82]
3	HF	700~800	200	48~96	Rapid-quench autoclave	5~20 μm	Solubility of molybdenite (MoS_2) in aqueous fluids	[70]
4	HF	700	140	96~120	Cold-seal pressure vessels	~50 μm	Solubility of tin in (Cl, F)-bearing aqueous fluids	[53]
5	HF	500~800	200	10~80	Cold-seal pressure vessels	>30 μm	Solubility of gold in oxidized, sulfur-bearing fluids	[56]
6	TS (450°C) + NaOH	800	500	80~96	Piston cylinder	>100 μm , max 1 mm	Solubility of monazite-(La) and xenotime-(Y) in H_2O -Na-K-Cl-F- CO_2 fluids	[71]
7	TS (550°C) + HF	600	100~200	336	Cold-seal pressure vessels	$n \sim >100$ μm	Combined LA-ICP-MS microanalysis of iodine, bromine and chlorine in fluid inclusions	[55]

Notes: "TS" designates the thermal shock prefracturing procedure with the temperature shown in parentheses.

TABLE 4: Some typical applications of the in situ fracturing FIS technique.

Number	T (°C)	P (MPa)	Run time (h)	High-temperature and high-pressure apparatus	Inclusion size	Applications	Literatures
1	700	200~600	/	/	/	Experimental determination of P-V-T-X properties in the CO_2 - H_2O system	[83]
2	700	140	168/72 ^a	Rapid-quench pressure vessels	10~20 μm	Solubility of tin in (Cl, F)-bearing aqueous fluids	[53]
3	1000	150	24/24 ^a	Rapid-quench (TZM) vessels	10~50 μm	Alkali metals control the release of gold from volatile-rich magmas	[69]
4	700~800	2500~2600	45~141/ 24~74 ^a	Piston cylinder	10~30 μm	Fluid-rock equilibria at the slab-mantle interface	[79]
5	650~900	90~130	24~72/ 24~96 ^a	Rapid-quench pressure vessels	10~30 μm	The partitioning of Cu, Au, and Mo between liquid and vapor at magmatic temperatures	[68]
6	800	200	24~144/ 36~72 ^b	Cold-seal pressure vessels	<10 μm	Solubility of gold in oxidized, sulfur-bearing fluids	[56]

Notes: run time such as "168/72" with superscript "a" indicates the time (168 h) for preequilibrium and that (72 h) for subsequent fracture healing after the in situ fracturing operation, respectively.

and densely interconnected fracture networks were produced as well. Fluid inclusions formed by fracture healing are secondary fluid inclusions and tend to concentrate along fracture planes especially where the fracturing is most intense. Rare primary inclusions are also seen in overgrowths on the original quartz prisms. The synthesized inclusions in general could display a wide range in morphologies, from very irregularly shaped to negative crystal-shaped. More isometric inclusions are probably formed at the intersection of thermal cracks. So far, the thermal shock

prefracturing FIS technique has been the most commonly used technique (see Table 1).

2.1.2. Preablating FIS Technique. The preablating technique was firstly reported by Loucks and Mavrogenes [4] in their study on the solubility of gold in supercritical hot brine (Table 2). The method requires a number of pits with a diameter of 30 to 100 μm and depth of 500 to 1000 μm , which are produced by ablating with a 193 nm excimer laser on a piece of selected transparent, inclusion-free quartz.

TABLE 5: Some typical applications of the in situ fracturing refilled FIS technique.

Number	T (°C)	P (MPa)	Run time (h)	High-temperature and high-pressure apparatus	Inclusion size	Applications	Literatures
1	500	70	24/72 ^a	Rapid-quench autoclave	20~40 μm , max 100 μm	Synthesize large fluid inclusions in quartz at controlled times and under unfavorable growth conditions	[82]
2	600~800	200	24~168/ 24~96 ^a	Rapid-quench autoclave	5~30 μm	Solubility of molybdenite (MoS_2) in aqueous fluids	[70]
3	800~850	200~230	24~192/ 24~120 ^a	Cold-seal pressure vessels	30~50 μm	Solubility of gold in oxidized, sulfur-bearing fluids	[56]

Notes: run time such as “24/72” with superscript “a” indicates the time (24 h) for pre equilibrium and that (72 h) for subsequent fracture healing after the in situ fracturing operation, respectively.

Once the preablated quartz piece is subjected to experiment, large primary fluid inclusions will be trapped preferentially in the pits and later sealed off by quartz overgrowth (e.g., fluid inclusion size $\geq 75 \times 500 \mu\text{m}$). The synthesized fluid inclusions by pit sealing are almost isometric and appear to be round or “neuron”-shaped, nearly without any necking down. Later, Dubessy et al. [81] successfully synthesized fluid inclusions in the $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$ system with the technique and introduced the formation of cavities and healing process related to the laser ablation in quartz in detail.

2.1.3. Preetching FIS Technique. The acid or alkali etching method was firstly adopted by Allan et al. [75], further introduced in detail by Duc-Tin et al. [53] who named it “etched plate technique” in their investigation on the solubility of Sn in aqueous solution (Table 3). In the method, quartz plates or pieces (e.g., $1 \times 2 \times 10 \text{ mm}$) are cut from inclusion-free quartz crystal by a rough rock saw, then immersed in concentrated hydrofluoric acid (30-40%) for 1 h to 2 h. By acid etching, a network of small etching channels on rough surface of the quartz plates is manufactured. Fluid inclusions formed by channel healing are secondary inclusions though their appearance resembles that of primary inclusions due to the unobvious healing channels. The synthesized inclusions are similar in morphology to that by fracture healing. One difference is that the fluid inclusions concentrate mainly at shallow depths below the surface. Likewise, some primary fluid inclusions would be entrapped on the surface during the overgrowing of new quartz. According to Duc-Tin et al. [53], a large number of quartz fluid inclusions about 50 μm in diameter were synthesized during 5 days within cold-seal pressure vessels under 700°C. Afterward, a similar etching method was successfully used by Li and Audétat [82] and Zhang et al. [70]. Given the fact that quartz is subject to react with hot strong alkali, the method of alkali pre-etching has also been employed (e.g., NaOH, [71]).

Lately, either two or three of the pretreatment methods have been combined as a composite method to further enhance efficiency and (or) synthesize large fluid inclusions. For example, the thermal shock and alkali etching methods were superimposed by Zhou et al. [71] to synthesize large fluid inclusions for determining the solubility of monazite and xenotime in specific fluids. Quartz was treated by thermal shock and then etched with 55 wt% NaOH solution at

160°C for about 16 hours. Abundant large fluid inclusions ($>100 \mu\text{m}$, individually up to 1 mm, see Figure 2(a)) were synthesized after 3 days at 800°C and 0.5 GPa in piston cylinder. A composite method combining the thermal shock prefracturing with the acid (HF) preetching was adopted as well by Fusswinkel et al. [55] in the synthesis of quartz-hosted fluid inclusions. Fluid inclusions synthesized by the composite method would be larger in size and tend to be more complicated in petrographic characteristics.

2.2. In Situ Fracturing FIS Technique. A knotty problem attached to the pretreatment FIS techniques is that the timing of fluid inclusion formation is uncontrollable due to the uncontrolled fracture healing, sealing, or overgrowth of the host [84, 85]. A series of issues would arise, such as fluid inclusion forming before the system reaching equilibrium, heterogeneous trapping, and thus compositional and volumetric heterogeneity of the synthetic fluid inclusions. Aiming to control the onset of fluid inclusion being trapped, an in situ fracturing FIS technique was invented by Sterner [85]. The new in situ fracturing FIS technique has the quartz fractured inside the pressure vessel at a certain time during the experiment so that the initial time of fluid inclusion development could be controlled by experimenters. The technique has greatly improved the precision of experiments for fluid inclusion synthesis, especially at temperatures above 600°C, and has been applied to some experiments involving slow kinetic buffers, diffusion processes, and water-rock interactions (e.g., [53, 56, 68–70, 79, 82], Tables 4 and 5). Given the close connection between in situ fracturing FIS technique and HTHP apparatus, the progresses of the in situ fracturing FIS techniques are outlined separately on the two principal apparatus (rapid-quench autoclave or pressure vessels and piston cylinder).

2.2.1. In Situ Fracturing FIS Technique Based on Rapid-Quench Autoclave/Pressure Vessels. In order to prevent premature fracture healing, Duc-Tin et al. [53] chose to apply in situ fracturing FIS technique in their investigation on the solubility of tin in (Cl, F)-bearing aqueous fluids. According to the authors, a capsule was charged with an intact quartz core, silica glass, and starting materials firstly and then sealed off; the sealed capsule was held in the upper part of the rapid-quench pressure vessels by a 25 cm long holder

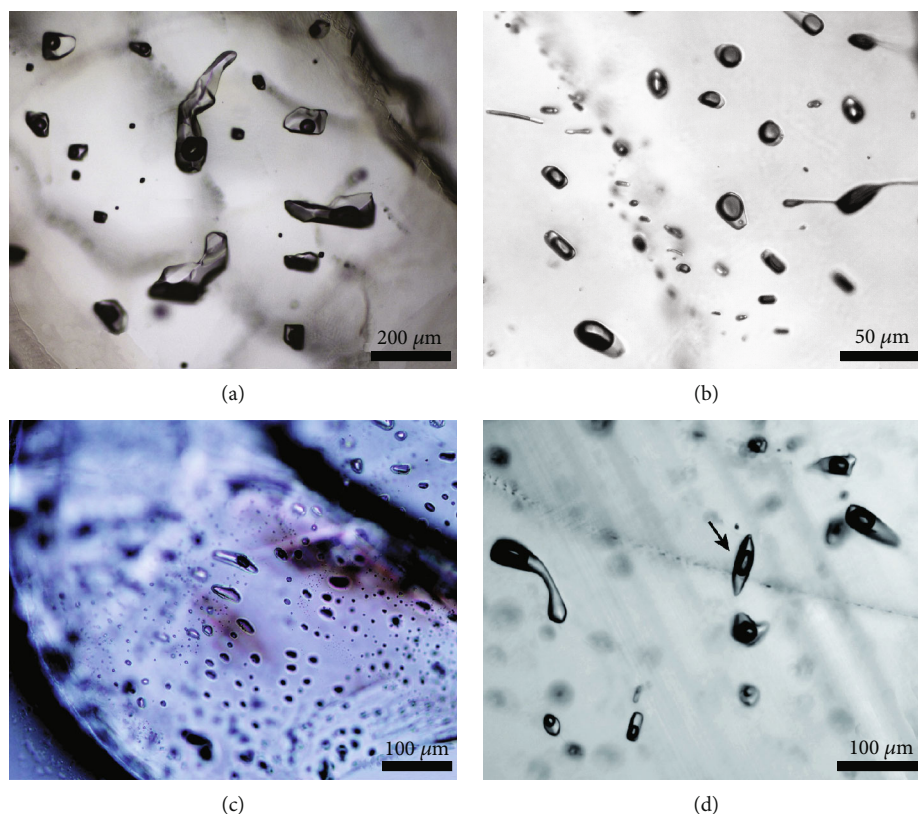


FIGURE 2: Microscopic photographs of the synthetic fluid inclusions with different FIS techniques. (a) Fluid inclusions synthesized by a composite method combining the thermal shock with alkali etching, cited from Zhou et al. [71]; (b) fluid inclusions synthesized by in situ fracturing FIS technique with rapid-quench autoclave, cited from [69]; (c) secondary fluid inclusions synthesized by in situ fracturing FIS technique with piston cylinders, cited from Tsay et al. [79]; (d) a large secondary fluid inclusion (pointed by arrow) synthesized by in situ fracturing refilled FIS technique, cited from Li and Audétat [82].

which itself could be moved from outside by a magnet. Subsequently, the loaded pressure vessel was brought to the desired temperature and pressure conditions and kept for a period of time till equilibrium was achieved. Importantly the capsule was pulled within 1 s to the cold end of the vessel with the magnet and then pushed back to the hot end, where they were kept for another period of time. The operation similar to nearly isobaric quenching would make the β -quartz transform to α -quartz in an instant (one to several seconds). Hence, numerous minor cracks in the quartz core were produced, some of which healed during the second period of time and thereby captured certain fluids. By the in situ fracturing FIS technique, Duc-Tin et al. [53] successfully synthesized many fluid inclusions which sampled fluid with homogeneous composition. A similar technique was employed as well by Zajacz et al. (see Figure 2(b), [68, 69]) and Guo et al. [56] to study the properties and behavior of gold and other metallogenic elements in magmatic-hydrothermal stage.

The progress of the in situ fracturing FIS technique relative to that reported by Sterner [85] mainly lies in the development of the apparatus. The in situ fracturing of quartz cores was formerly accomplished by rotating the pressure vessel together with furnace through the necessary orientation, which usually took several minutes to complete [85]. Now, the similar in situ fracturing could be completed by

simply moving a magnet within several seconds as described above ([53, 69]).

2.2.2. In Situ Fracturing FIS Technique Based on Piston Cylinder. Previous experiments show that the thermal shock induces significant fractures at lower or atmospheric pressure range across the α - β quartz transition. However, attempts to in situ fracture the quartz crystal by sudden quenching and reheating during the experiment within the stability field of α -quartz were not successful [79]. To implement in situ fracturing FIS technique at conditions within the stability field of α -quartz, Tsay et al. [79] proposed a viable measure that the pressure and temperature of the experiment were cycled across the boundary between α -quartz and coesite, as shown schematically in Figure 3. The steps are as follows: (1) have the starting materials in the capsule reacted for a while to get equilibrium at designed temperature and pressure; (2) raise pressure under the fixed temperature so that the α -quartz would transform to coesite (0.7~0.8 GPa higher than that of the transition point) and maintain for several hours to complete the phase transformation (be cautious to prevent reequilibration of the system at higher pressure); (3) swiftly bring down the temperature to $\sim 300^\circ\text{C}$, which would induce a sudden decompression resulting from relatively large amount of aqueous fluid in the experimental capsule and the thermal expansion/

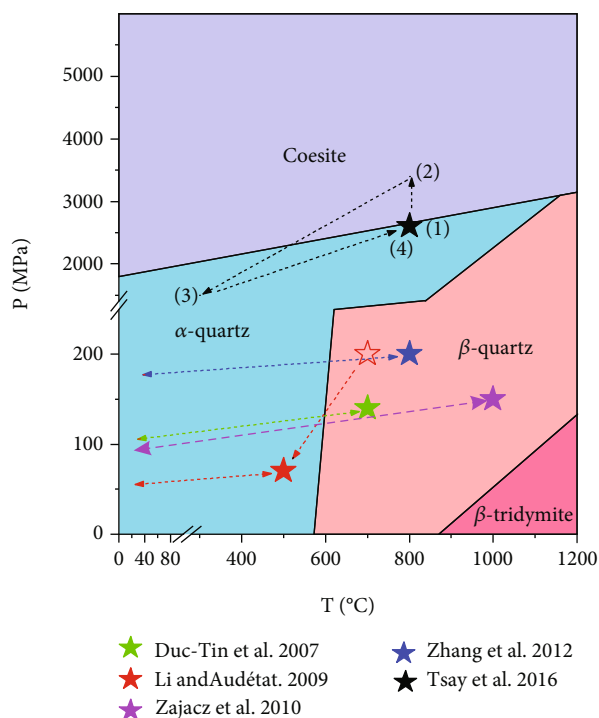


FIGURE 3: Schematics of the in situ fracturing and the in situ fracturing refilled FIS techniques. Notes: stars indicate the temperature and pressure conditions of the experiments; dashed lines and arrows with or without numbers show the rough P-T paths and directions of the experiments. The green star, green dashed line, the magenta star, and the magenta dashed line illustrate the in situ fracturing FIS technique employed by Duc-Tin et al. [53] and Zajacz et al. [69], respectively. The red stars (solid and hollow), red dashed lines, and arrows simply illustrate the in situ fracturing re-filled FIS technique reported by Li and Audétat [82]. The hollow star represents the condition of a separate experiment, specially chosen to be higher than that of the second experiment. The blue star and blue dashed line show the in situ fracturing refilled FIS technique applied by Zhang et al. [70] in the same experiment at the second step as that at the first step. The black star, black dashed lines, and arrows with numbers illustrate the in situ fracturing FIS technique adopted by Tsay et al. [79].

contraction of the entire piston-cylinder assembly; and (4) adjust temperature and pressure back to the initial value, under which the capsule is maintained for another while till the desired fluid inclusions are entrapped in the quartz during healing of the in situ fractures. Steps 3 and 4 are typically done in a few seconds. The main purpose of step 3 is to ensure relatively fast transition of coesite to α -quartz and thus large number of in situ fissures being produced in the quartz. It has been demonstrated by Tsay et al. [79] that the secondary fluid inclusions formed by the prefracturing FIS technique are systematically diluted and probably be entrapped at the early stage in the experiment, while those synthesized by the in situ fracturing FIS technique sampled the most representative equilibrium fluid at high-pressure and high-temperature conditions (see Figure 2(c)). Furthermore, this in situ fracturing FIS technique extends the applicable conditions to near the quartz-coesite phase boundary,

and it also enhances the reliability of the quartz FIS technique under the extreme conditions relevant to slab dehydration beyond crustal depths. Fluid inclusions formed by the two in situ fracturing techniques are basically not different from those by the prefracturing technique in petrographic characteristics.

2.3. In Situ Fracturing Refilled FIS Technique. With the rapid development of LA-ICP-MS [75, 77, 86–88], the in situ LA-ICP-MS analysis of individual fluid inclusion has been recognized as a sensitive, efficient, and robust approach, which has also contributed to the increasing use of the FIS techniques in element solubility and (or) partitioning studies. However, the practice of individual fluid inclusion analysis by LA-ICP-MS indicates that relative larger inclusions are more suitable for the determination of element concentrations in the parts per million range in fluids of low density and salinity, even with optimized sensitivity [86]. In addition, experiments involving element solubility and partitioning commonly require a long time to achieve equilibrium, which means the accurately controlled timing of fluid entrapment is essential. Based on the two requests (large fluid inclusion and controlled timing of fluid entrapment), Li and Audétat [82] reported a new technique that combines the advantage of the prefracturing FIS technique with that of the in situ fracturing FIS technique (Table 5).

The technique is a two-step approach, in which large fluid inclusions are produced during a first step and then reopened and refilled with new fluid during the other step (illustrated in Figure 3). In the first step, numerous large fluid inclusions are synthesized by the acid prefracturing FIS technique during a first-step experiment. In the second step, the recovered quartz containing presynthesized fluid inclusions from the first step is loaded into a capsule together with the experimental starting materials. Subsequently, the charged capsule is subjected to a second-step experiment, in which the in situ fracturing FIS technique as described in Section 2.2.1 is adopted. Numerous in situ cracks would be developed in the quartz due to the in situ fracturing procedure, and some of those presynthesized inclusions in the quartz would be reopened by in situ fractures. At each location where a crack intersects a presynthesized fluid inclusion, the original fluid content of the inclusion would be replaced by the new equilibrium fluid in the capsule. Fluid inclusions synthesized by the in situ fracturing refilled technique are secondary inclusions. They usually have regular shape or negative crystal shape because of adequately long time for necking down. Actually, the second-step experiment is our ultimate target, which has much close relation to the specific investigation. The first-step experiment could be an independent experiment with different temperatures and pressures (e.g., [82]) or be the same one as the second-step experiment (e.g., [56, 70]). In the attempting experiments, Li and Audétat [82] chose a distinct first-step experiment with higher temperature and higher pressure (see Figure 2(d)). The results showed that numerous large fluid inclusions were successfully synthesized at unfavorable conditions and the timing of fluid inclusion entrapment was well controlled. Afterwards, the in situ fracturing refilled

FIS technique was successfully used by Zhang et al. [70] and Guo et al. [56] in solubility studies.

2.4. Fused Silica Capillary FIS Technique. The fluid inclusions synthesized by fused silica capillary FIS technique have many similarities with those synthesized by traditional methods even if the host is represented by silica capillary instead of quartz. Therefore, the fused silica capillary FIS technique is also incorporated in this review. The fused silica capillary FIS technique was firstly reported by Chou et al. [89] in their study on laser Raman probe correction, then was further improved and applied to a series of researches about the properties of geological fluids and fluid inclusions by Chou and his team [5, 90–93]. The technique was also applied by Chen and Ge [94] for synthesizing hydrocarbon-bearing inclusions and employed by Ni et al. [95] to synthesize fluid inclusions in the systems of pure H₂O, pure CO₂, H₂O-NaCl, and H₂O-CO₂.

In the fused silica capillary FIS technique, a set of sample loading system is indispensable (see Figure 1 in Chou et al. [5]). The fused silica capillary tubing has either a square or round cross-section, with dimensions ranging from 0.15 to 0.80 mm in outer diameter and 0.002 to 0.70 mm in inner diameter. Organic or inorganic samples in solid or liquid forms are first loaded into a special capillary tube (about 6 cm long with one end sealed), which is then centrifuged to force the sample into the closed end with a high-speed (14,000 rpm) microcentrifuge. To protect the fragile sample tube, it is inserted in a protective glass tube before centrifugation. After centrifugation, the open end of the tube is connected to a pressure line to evacuate the air in the sample tube. Subsequently, gaseous samples are added to the tube by switching the pressure line from vacuum to sample gas at about 0.2 MPa pressure, simultaneously with the sealed end of the tube immersing in liquid nitrogen. The gaseous component is allowed to condense or freeze to a solid in several minutes. Finally, the tube is evacuated and sealed at the open end by fusion in a hydrogen flame while frozen and under vacuum. It is reported that the novel FIS technique provides a new and reliable measure for the experimental study of geological fluids and fluid inclusions.

2.5. Pros and Cons of the FIS Techniques

2.5.1. The Pretreatment FIS Techniques. In all kinds of the pretreatment FIS techniques, the purpose of the pretreatment procedure is to produce fractures (or channels, pits) in quartz and thus to facilitate fluid entrapment as inclusions by fracture healing or quartz overgrowth. The dimensions, depth, numbers, and density of the fractures (or channels, pits) are mainly determined by the adopted pretreatment procedures, which significantly affect the fracture healing and sealing [38, 84, 96, 97] and thus have a major impact on the size, quantities, occurrence, and morphology of the fluid inclusions synthesized.

The thermal shock prefracturing method is the most frequently used due to some advantages. Firstly, it is simple and efficient. Using this method, quartz can be processed in batches while a large number of closely spaced fractures

could be easily produced without disintegrating quartz. Secondly, the numerous fracture planes are usually perpendicular to the long axis of the quartz, which provides ideal localities for inclusion synthesis and is convenient for later microscopic observation. In addition, it usually takes a shorter duration to synthesize inclusions by fracture healing than by quartz overgrowths under the same conditions. However, fluid inclusions synthesized by healing fractures are secondary inclusions and relatively smaller than those in the overgrowths according to Bodnar et al. [40].

In the laser preablating method, the size, quantities, and density of denudation pits can be accurately controlled so that the desired big, isolated fluid inclusions could be obtained. However, the quartz ablation must be done pit by pit and piece by piece, which made it tend to be inefficiency. Meanwhile, the process is prone to be affected by many factors (e.g., laser spot size, laser frequency, and energy density, [98, 99]). It is reported that slightly high laser energy can easily lead the quartz crashing due to its brittleness. Furthermore, related studies show that longer time for pit sealing is required than that for fracture healing by the prefracturing FIS technique (e.g., at 625°C and 370 MPa, [4]). In conclusion, the laser preablating method is relatively costly and time-consuming.

In the acid or alkali preetching method, the concentration of acid or alkali solutions, temperature, and etching time are crucial factors impacting the effectiveness. Deep, narrow etched channels (>100 μm in depth) always occur without orientation at the surface rather than the interior of quartz. Quartz could be processed in batches with the preetching method, which could also be combined with the other pretreatment methods. It is noted that certain acid or alkali solution (e.g., hydrofluoric acid) is subject to induce environmental hazards and (or) contamination.

All the pretreatment FIS techniques have been verified to be effective. However, the pretreatment FIS techniques in principle have a common drawback that the probable premature fracture healing or quartz overgrowth before the final conditions and (or) the equilibrium being reached. The premature fracture healing or quartz overgrowth would result in unrepresentative fluid being captured and/or volumetric and compositional heterogeneity among inclusions from a single sample. Nevertheless, these techniques are more than practical in some experiments at relatively low temperature (<600°C) or in experiments with fluid components fast mixing or rapidly to equilibrium [64, 85].

2.5.2. About the In Situ Fracturing FIS Technique. The in situ fracturing FIS technique has been testified to produce a large number of compositionally and volumetrically homogeneous fluid inclusions within a single sample. The in situ fractured quartz is always with much greater fracture density, smaller individual fractures, and apparently random fracture orientation compared with those by the thermal shock. Such in situ fractures rarely penetrate the quartz deeper than 1.0–1.5 mm and therefore present no difficulties in the following sample preparation [85]. The in situ fracturing procedure has been well adopted at experimental temperatures above 600°C (see Table 1).

Though can be maximum mitigated, a few weaknesses are there. Firstly, at temperatures above 700°C, fracture density would become so large that inclusions are literally stacked on top of each other, which is unfavorable for the following individual fluid inclusion analysis. The inclusion density can be reduced by increasing the pressure moderately during the fracturing procedure, while the risk of capsule rupture would be increased due to the additional deformation experienced. Secondly, a relative smaller number of inclusions and thus less measurable inclusions would be obtained than those by the prefracturing FIS technique. However, it is reported that the number of measurable inclusions occurring on independent fractures is regularly greater and most inclusions along a single fracture plane are of nearly identical composition and bulk density. Thus, the number of measurements from independent fracture planes is more important than the total number of inclusions. In addition, disturbance from temperature and pressure cycling would arise.

Although it often takes longer time to synthesize fluid inclusions (an extra period of time for preequilibrium) with the in situ fracturing FIS technique, the more representative fluids would be sampled and thus, the relevant meticulous researches are greatly improved. Furthermore, it is important to be emphasized that the in situ fracturing FIS technique is closely related to high-temperature and high-pressure experimental apparatus. The in situ technique was rightly invented on the basis of the rapid-quenching function of the autoclave or piston cylinder. Therefore, the progress of the in situ fracturing technique needs the innovation of high-temperature and high-pressure experimental equipment.

2.5.3. About the In Situ Fracturing Refilled FIS Technique.

The in situ fracturing re filled FIS technique invented by Li and Audétat [82] provides an ideal solving to the experiments, in which large fluid inclusion needs to be synthesized under unfavorable conditions (e.g., at temperature $\leq 500^\circ\text{C}$) and the timing of the coexisting fluid being entrapped requires to be controlled. Critical issues, like whether the primary fluid inclusions could be reopened by in situ cracks and whether the contents of the primary fluid inclusions could be completely replaced by the new equilibrium fluid, have been confirmed to be insignificant by the testing experiments. Primary fluid inclusions and the refilled ones were synthesized simultaneously in the experiments, with the latter intersected by in situ cracks (Figure 2(d)), and that all the reopened inclusions were filled with the new fluid according to the calculated fluid replacement efficiency ($>97.5\%$). As suggested, the fluid replacement ratios could be raised by repeated in situ fracturing procedures, any contribution from the previous residual fluid could easily be subtracted mathematically, and primary fluid inclusions could also be reopened by a large pressure drop instead of thermal quenching. However, a large pressure drop would probably result in negative effects such as decrepitation of the synthesized fluid inclusions due to high inner pressure and thin in situ fractures which tend to be sealed so immediately that there is not enough time for the new fluids to replace the

old ones in the inclusions. Pressure drops are likely to result in fluid immiscibility if the run conditions are close to the solvus of the fluid. Besides, the compositions of the refilled inclusions are generally better reproduced than those of the primary fluid inclusions according to Zhang et al. [70].

The main disadvantage of the technique lies in the relatively complex operation, such as two-step experiments, recovery, and reuse of the quartz crystals. In addition, special attention needs to be paid to some issues, such as whether the fractures healed before the fluid reattained equilibrium with respect to all solids and whether the selective diffusion of elements between the primary and the refilled secondary fluid inclusions have any effect on the composition of equilibrium fluids represented by the refilled fluid inclusions (e.g., Na; [82]).

2.5.4. About the Fused Silica Capillary FIS Technique.

According to Chou et al. [5], almost any fluid inclusion with a known, fixed composition can be synthesized by the fused silica capillary FIS technique. The components that can be loaded include solids, liquids, and the majority of gases easy to be condensed or frozen by liquid nitrogen. Based on the peculiarity, the technique can be utilized to a wide range of problems of interest in fluid inclusion and hydrothermal research, such as creating standards for the calibration of thermocouples in heating-cooling stages and frequency shifts in Raman spectrometers. The fused silica capsules can also be used as containers for hydrothermal reactions, especially for those with organic materials involved. Compared with the former described FIS techniques, the new fused silica capillary FIS technique has some advantages. The technique is simple and especially suitable for the study of organic material, by which the synthesized fluid inclusions are large, uniform, and able to tolerate high internal pressure [5].

However, it is also the unique pattern of the fluid inclusion synthesis that makes the fused silica capillary FIS technique lose an important function, in situ sampling of the HTHP fluids. Besides, the morphologies of the synthetic fluid inclusions are distinctive, tending to be longer along the capillary direction (~ 25 mm in length, see Figure 2 in Chou et al. [5]). Such fluid inclusions are more suitable for microthermometric measurements and Raman analysis, rather than LA-ICP-MS analysis.

3. Notes and Prospects of the FIS Techniques

3.1. Notes of the FIS Techniques. Quartz used as the most prevailing host mineral is logical for several reasons as listed by Sterner [85], such as widespread occurrence in nature, moderate solubility, stable physical and chemical properties, and special strength. Although other host minerals (e.g., calcite, olivine, pyroxene, halite, corundum, and plagioclase) are also used in FIS techniques [100–105], quartz remains the most extensive choice. As the most widespread participator or witness in various geological processes in the crust and upper mantle, so many mysteries of science need to be disclosed by quartz FIS techniques. However, some problems need to be paid attention to in practical applications.

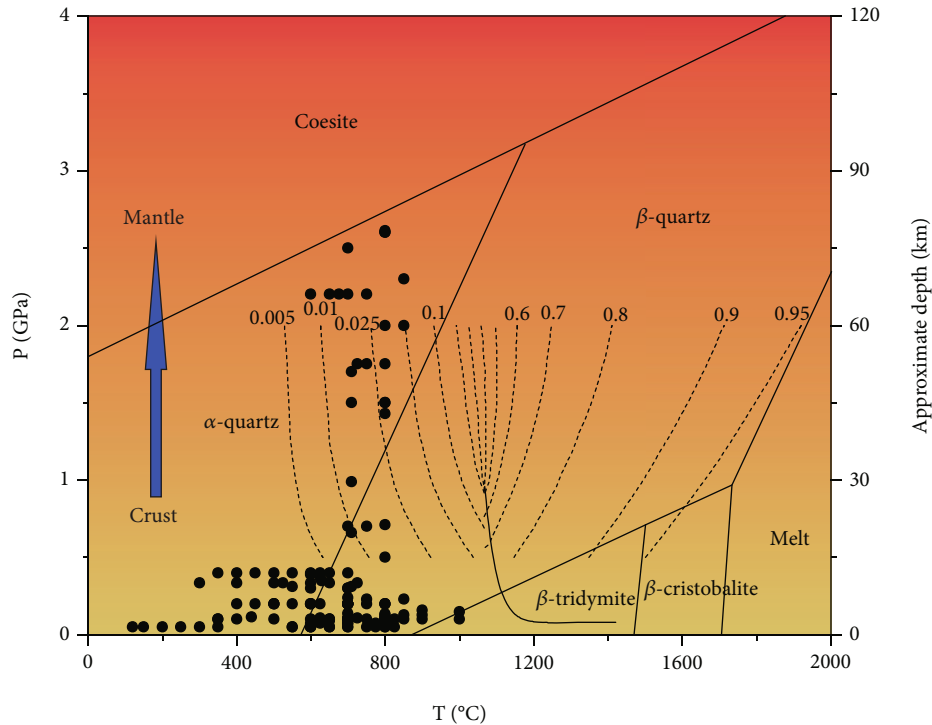


FIGURE 4: Temperature and pressure plots of some typical applications of the FIS techniques. Notes: black solid circles show the temperature and pressure conditions of the typical experiments for fluid inclusion synthesis. The related temperature and pressure data are mostly from literatures listed in Tables 1–5 and in the reference list [30, 36, 43, 44, 47]. Dashed lines are the isopleths of the quartz solubility in pure water, and the values are expressed mole fraction [106]. The heavy solid line represents the wet quartz melting curve according to Kennedy et al. [107]. The phase diagram of silica is modified after Ford et al. [108] and Mao et al. [109].

3.1.1. The Scope of Application. The quartz FIS techniques are only suitable for quartz- (or silica) saturated systems, which has already been emphasized by many pioneers (e.g., [1, 40, 79, 85]). In the experiment, quartz is always loaded together with a certain amount of silica gel or powder so that the system is silica saturated, which facilitates the silica gel or powder dissolution first and then reprecipitation on the quartz. It is the precipitation of quartz that leads the fracture sealing or quartz overgrowth and the fluid inclusion entrapment. Consequently, the techniques should be never applied to quartz (or silica) unsaturated systems.

The quartz FIS techniques have been used mostly at the stability field of α -quartz, secondly at the stability field of β -quartz (see Table 1 and Figure 4), with a few at the field near that of coesite (representing the conditions close to the lower crust, upper mantle, and subduction zones; see Table 1). According to Figure 4, there are many blanks to be explored for the quartz FIS techniques. However, fluids in certain fields of the silica phase diagram are possibly immiscible with two or more coexisting phases, which would lead to heterogeneous trapping. Although the heterogeneous trapping of the synthetic fluid inclusions has been utilized for special researches by some geochemists (e.g., [40, 56, 64, 68]), the complexity should be paid adequate attention to in practice. Likewise, geofluids at the temperature and pressure conditions in certain fields probably lack geological significance. In addition, the quartz hollow fractures tend to close instantly as the pressure increases, which makes it dif-

ficult to capture the fluid. Excessive pressure also causes the formed fluid inclusions difficult to be preserved. The reported wet quartz melting curve by Kennedy et al. [107] also sets the limitations for the application of quartz FIS techniques.

3.1.2. The Probable Effects from the Host Mineral (Quartz).

Effects from the host mineral (quartz) on fluid inclusions should be paid extra attention in certain cases. It is an undoubted fact that quartz would dissolve into the fluid at high temperature and high pressure. Figure 4 shows the quartz solubility in pure water as a function of temperature and pressure. At low temperatures ($T < \sim 800^\circ\text{C}$) the quartz solubility is relatively small and thus, the effect on the fluid could be ignored. However, the solubility of quartz increases drastically at higher temperature ($T > \sim 800^\circ\text{C}$), which would become even higher in chloride-bearing solutions than in pure water [30, 40, 110, 111]. In fact, numerous kinds of geofluids in nature are much closer to chloride-bearing solutions. Under such circumstances, the effect of quartz dissolution must be assessed cautiously. Besides the effect, the possible interaction between quartz and salt-water may exert an effect on fluid equilibria, which was discussed by the pioneers as early as in their first publications [40, 85] and was confirmed by the observation of glasslike phase in some of the synthetic fluid inclusions [30]. Quartz probably does not remain inert with respect to salt-water system under certain conditions.

3.2. *The Prospects of the FIS Techniques.* Some microanalytical techniques can be combined with FIS techniques for accurately characterizing the compositional and volumetric properties of the HTHP fluids. Techniques such as LA-ICP-MS, multicollector ICP-MS (MC-ICP-MS), particle-induced X-ray emission (PIXE), synchrotron X-ray fluorescence (SXRF), and X-ray absorption near-edge structure (XANES) spectroscopy are all suitable for obtaining information from individual inclusions. XANES has the advantage of allowing the speciation in the fluid inclusions to be determined. Notably the LA-ICP-MS analysis of individual fluid inclusions offers possible advantages, including high spatial resolution, high sensitivity, high precision, low detection limit, and multielement or isotope simultaneous quantification. The quartz FIS technique combined with microanalytical techniques has become a powerful tool to obtain information of the HTHP fluids and made the studies tend to be much more accurate and more refined. (e.g., [4, 35, 50, 53, 55–62, 65, 66, 68–71, 75, 79, 82, 112]).

Experienced nearly 40-year development, the quartz FIS techniques have formed a set of methodologies and have been applied in a large number of investigations involving many fields, with which fruitful accomplishments have been achieved. During the last decades, the versatility of the FIS techniques makes these techniques the method of choice for kinds of research, such as solubility, speciation, mobility and partitioning of selected elements (Na, K, U, Th, La, Y, Cu, Au, Mo, and Sn), fluid–rock interaction, trace element release during ultrahigh-pressure serpentinite dehydration, and the state of the water in Earth’s mantle (e.g., [50, 55, 56, 65, 68–71, 79]).

In conclusion, the FIS technique has become a powerful tool to realize the fluid in situ sampling under high-temperature and high-pressure conditions and thus precisely characterize the HTHP fluids. Based on the scientific research tending to be more refined and precise, it is predicted that the in situ fracturing and (or) relatively large-volume synthetic fluid inclusions will probably be an important future direction.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

Honglun Chang and Jun Du had the idea for the article; Jun Du, Hongwei Liu, and Honglun Chang performed the literature search and data analysis; Jun Du, Hongwei Liu, and Honglun Chang drafted; and Jun Du critically revised the work.

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