Review

The Role of Fluids in Melting the Continental Crust and Generating Granitoids: An Overview

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Abstract: Granite is a distinctive constituent part of the continental crust on Earth, the formation and evolution of which have long been hot research topics. In this paper, we reviewed the partial melting processes of crustal rocks without or with fluid assistance and summarized the role of fluids and volatiles involved in the formation of granitic melts. As a conventional model, granitoids were thought to be derived from the dehydration melting of hydrous minerals in crustal basement metamorphic rocks in the absence of external fluids. However, the external-fluid-assisted melting of crustal metamorphic rocks has recently been proposed to produce granitoids as extensive fluids could be active in the deep continental crust, especially in the subduction zones. It has been demonstrated experimentally that H2O plays a crucial role in the partial melting of crustal rocks, in which H2O can (1) significantly lower the solidus temperature of the melted rocks to facilitate partial melting; (2) affect the melting reaction process, mineral stability, and the composition of melt; and (3) help the melt to separate more easily from the source area and aggregate to form a large-scale magma chamber. More importantly, dissolved volatiles and salts in the crustal fluids could also lower the solidus temperature of rocks, affect the partitioning behaviors of trace elements between minerals and melts, and facilitate the formation of some distinctive granitoids (e.g., B-rich, F-rich, and high-K granitoids). Furthermore, various volatiles dissolved in fluids could result in elemental or isotopic fractionation as well as the diversity of mineralization during fluid-assisted melting. In-depth studies regarding the fluid-assisted partial melting of crustal rocks will facilitate a more comprehensive understanding of melting of the Earth’s crust, thus providing strong theoretical constraints on the genesis and mineralization of granitoids as well as the formation and evolution of the continental crust.

Keywords: fluids; partial melting; volatiles; dehydration melting; granitic melt

1. Introduction

Granite is one of the most widely distributed rocks on the continental crust, and it is also a common component of the upper continental crust on Earth [1,2]. Serving as a host of several major mineral resources, granitoids could also be divided into common and rare-metal groups [3–6]. The processes involved in the formation of granitoids are usually associated with tectonic events, magma differentiation, and even mineralizing processes [7–13]. Consequently, understanding the genesis and evolution of granitoids is crucial and meaningful.

Although studies regarding the formation of granitoids already span two centuries—from the earliest arguments between Neptunism and Plutonism to the controversy between metamorphic and magmatic origins—granitic genesis remains controversial. It was previously thought that granitic magma was the product of mantle-derived magma which experienced extensive fractional crystallization and chemical differentiation. Subsequently, the concept that granitoids mainly originate from the partial melting of crustal metamorphic basement rocks was proposed [14–23]. The earliest evidence of this idea can mainly be
attributed to the Qz-Ab-Or ternary melting experiment conducted by Tuttle and Bowen in 1958. This experiment confirmed that granitic melts can form under high hydrostatic pressures and relatively low temperatures (<700 °C), which implies that it is very likely that appreciable granitic magma is generated via partial melting at the continental crustal depths [24]. Furthermore, other experiments regarding the melting of mantle-derived peridotite demonstrated that the melting of mantle rocks is not directly associated with the generation of granitic magma, but with the formation of basaltic magma, such as MORB. The basalt undergoing partial melting could be capable of forming specific I-type granitoids [12,25–30]. In contrast, in experiments regarding the partial melting of crustal rocks, it was shown that this type of melting can generate almost all types of granitic melts [8,20,31–36]. Therefore, the concept that granitic melts mainly originate from the partial melting of the continental crust was widely accepted. Varied conditions, such as the crustal rock’s composition, source heterogeneity, temperature, pressure, degree of partial melting, and other processes involved in partial melting, are sufficient for the formation of various granitoids [37,38]. Experimental petrology and geodynamic modeling studies have also shown that the melting of crust rocks can result in large-scale magmatism [8,20,21].

Experimental results regarding the partial melting of natural crustal basement rocks or synthetic materials provide direct evidence for and constraints concerning the formation of granitoids. Since the earliest melting experiment on the Qz-Ab-Or ternary system was carried out by Tuttle and Bowen in 1958, most melting experiments have been conducted under water-supersaturated conditions and with synthesized water-saturated granitic melts [39–41]. In contrast, granitic magma was once considered to form in anhydrous environments, given the low water content of natural rock and the fact that the crust was dry [42,43]. Therefore, since the 1980s, numerous experiments on the dehydration melting of hydrous minerals in crustal rocks were conducted without adding water. The dehydration melting of hydrous minerals does explain some issues in the formation of granitoids and can generate considerable amounts of granitic magma. Previous studies proposed that, implicitly or explicitly, the granitoids generated via crustal melting are the result of dehydration melting reactions. However, Aranovich et al. (2014) discovered that most granitic melts equilibrated with proportions of quartz and feldspar contained at least ~3–4 wt.% H$_2$O [44]. However, the granitic melts produced by the dehydration melting of hydrous minerals in crustal rocks alone are not sufficient to supply water for the formation of large granitoid batholiths [22]. With the development of geophysics and research into fluid inclusion, it was found that extensive fluid activities still take place even in the deep continental crust with low permeability, especially in the subduction zones [37,45–52]. The fluids in the crust, more or less, could participate in the partial melting of crustal basement rocks. As a result, the model of fluid-assisted partial melting also gradually began to gain interest [53–56]. The role of fluids during the partial melting process is sometimes considered to be extremely subtle, such as a slight change in the activities of the water or the volatile component [57–59]. More importantly, the role of fluids is sometimes considered to be noticeable. Fluids can obviously change the solidus temperature of rock [56,60–62], as well as mineral stability and reaction pathways during the partial melting process [61–64]. Additionally, the distribution of trace elements and isotopes among various phases could be controlled by the composition of fluids [59,65,66].

In this paper, we mainly summarize the published experimental results conducted to examine the partial melting of crustal rocks without or with fluid assistance. Furthermore, we provide an overview of the effect of water and volatiles on crustal partial melting and compare the behaviors of various fluid components to discuss the roles of fluids in the formation of granitic melts, aiming to provide some direction or suggestions for further research.

2. Fluid-Absent Partial Melting

The fluid-absent partial melting of crustal rocks was a hot topic in the 1980s. Most of the experiments mainly focused on, but were not limited to, solidus temperatures,
dehydration melting reactions, the influence of hydrous mineral components, the effects of temperature and pressure on melting, and so on. Under fluid-absent conditions, the partial melting of rocks mainly involves the dehydration processes of hydrous minerals which supply all of the water to the reaction systems.

Table 1 lists the possible dehydration melting reactions of crustal rocks. The dehydration of hydrous minerals in pelitic and felsic metamorphic rocks mainly relies on the presence of muscovite and biotite, while in intermediate and basic metamorphic rocks, it is mainly controlled by the existence of biotite and amphibole. Broadly, we generally consider S-type granites to be sedimentary or metasedimentary in origin, so the dehydration melting reactions concerned with micas mainly generate S-type granitic melts. The I-type granitic melt, which we consider to be igneous or metaigneous in origin (especially basic rocks), mainly result from the dehydration melting of amphibole. When only depending on hydrous minerals, the dehydration melting of pelitic rocks rich in hydrous minerals was capable of generating 30 vol.% water-undersaturated magma [43,67].

Table 1. Possible dehydration melting reactions of the crustal rock.

| Melting Reaction | Rock Type     | References                      |
|------------------|---------------|---------------------------------|
| Ms + Ab + Qz = Kfs + Als + melt | pelite | Petö (1976) [68]                  |
| Ms + Pl + Qz = Kfs + Als + Bt + melt | pelite | Patiño Douce and Harris (1998) [69] |
| Bt + Pl + Q = Opx + Crd + melt (lower pressure) | metagreywacke | Vielzeuf and Holloway (1988) [70] |
| Bt + Pl + Q = Opx + Grt + melt (higher pressure) | greywacke | Conrad (1988) [71]               |
| Bt + Pl + Q = Hb + Grt + melt |        |                                 |
| Amp + Pl + Qz = Cpx + Op + Mag + melt | basalt | Beard and Lofgren (1991) [72]           |
| Amp + Pl + Cpx + Op + Grt + melt (1 GPa) | amphibolite | Wolf and Wyllie (1994) [73]          |
| Amp + Pl = Grt + Cpx + Melt (2 Gpa) | amphibolite | Zhou (2005) [74]                     |

It is well known that the dry solidus temperature of rock is usually higher than the dehydration temperatures of hydrous minerals. For example, the dehydration temperature of pure muscovite is usually around 700 °C at a pressure of 0.5 GPa [75], which is lower than the dry solidus temperatures of pelitic rocks (Figure 1). The water produced by the dehydration of hydrous minerals will greatly reduce the solidus temperatures of rocks and then promote the decomposition and melting of other minerals such as feldspar and quartz, resulting in the generation of more magma [76].

The dehydration and decomposition temperature of biotite is normally higher than that of muscovite, while amphibole can maintain its structural stability at comparatively higher temperatures. When the melting temperature of hydrous minerals cannot be reached, the whole rock system is equivalent to an anhydrous system, which is also the reason why the solidus curve of some rocks partially overtops or coincides with the melting curves of hydrous minerals.

Burnham (1975) considered that the formation of melt was constrained by the amount of available water [80]. In other words, at specific temperature and pressure conditions, the amount of melt produced is usually closely related to the types and contents of the hydrous minerals in the rocks. Clemens and Vielzeuf (1987) and Rushmer (1991) thus established the relationship models between the maximum amount of melt that can be produced by different types of rocks and the water contents in hydrous minerals [16,43] (Figure 2). Based on these models, we can intuitively understand the influences of various factors on the amount of melt that can be produced during the melting process. For example, pelites and felsic rocks with a total water content of ~1 wt.% can form about 30 vol.% melt at 0.5 GPa and 800 °C, and intermediate rocks with a total water content of ~1 wt.% can form up to 25 vol.% melt, whereas mafic rocks can only form less than 20 vol.% melt. This also indicates that the potential of producing melt gradually drops from felsic to basic rocks under the same environmental conditions. Moreover, the increase in temperature and the
decrease in pressure will increase the amount of melt produced from whole-rock systems, but the maximum amount of melt produced is usually limited by H$_2$O in hydrous minerals.

Figure 1. The representative dry or wet solidus curves of the crustal rocks and dehydration temperature of hydrous minerals, modified after the references [54,77–79].

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Figure 2. The effect of water on the melt volume derived from partial melting of crustal rocks. The number represents the water content (wt.%) for the whole rock. The thick line shows the melt volume as a function of temperature and initial water contents of protolith in fluid-absent melting reactions of some crustal rocks at 0.5 GPa [16,43], which represents the maximum amount of melt derived from the rock’s partial melting. The thin solid line and dashed out line, respectively, show the melt volume as a function of temperature for various H$_2$O-absent or H$_2$O-present starting compositions in experiments [81–84].

Hacker and Liou (1998) once pointed out that the dehydration of hydrous minerals is a restricted condition for crustal melting [85]. It can be considered that in this case, all water required to reduce the solidus of rock and the water in melt are provided by the breakdown of hydrous minerals, and the limited amount of water will greatly restrict the production of the melt. Therefore, the reduction in solidus and the promotion of melt production driven by water play crucial roles in the genesis of granitoids and the evolution of the whole crust.

3. Fluid-Assisted Partial Melting

Geophysics and fluid inclusion studies have already confirmed the existence of fluids in the deep crust, especially in the subduction zones. These fluids are mainly dominated by H$_2$O-CO$_2$ compounds and may also include varying quantities of halogens, alkalis, and dissolved silicates [4,22,47,86–91].

Water, a medium which reduces the activation energy, is a solvent that dissolves volatiles and salinity, and it plays a considerable role in the formation and evolution of granitic magma [67,92,93]. The external-fluid-assisted melting (also known as water-fluxed melting or water-present melting) of crustal rocks might facilitate the continental crust’s differentiation process. The most direct effect of external water during the partial melting of crustal rocks is that it greatly reduces the restrictions on the rock melting and produces a larger amount of melt (Figure 2). Ebadi and Johannes (1991) studied the relationship between H$_2$O activity and the solidus of a simple granite system and found that the solidus temperature of granite gradually decreased as the H$_2$O activity increased from 0 to 1 [94]. Moreover, when H$_2$O activity slightly rose from 0, the solidus temperature began to decrease significantly. Figures 1 and 2 also show that the temperature of the wet solidus
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Experimental results have also proven that in the presence of fluids, the temperature required to produce considerable amounts of melt will be reduced by 100~200 °C [33,82,95], even though only a small amount of water (1~2 wt.%) may significantly affect the production of melt [96]. Gardien et al. (2000) found that biotite-plagioclase-quartz gneiss could only form a small amount of melt at 900 °C under anhydrous conditions, whereas adding 4 wt.% water could produce substantial melt (70~80 vol.% [33]. Droop and Brodie (2012) also observed that for pelitic rocks, only a small amount of melt was produced in the absence of fluids, but a higher degree of melting could be achieved due to the addition of a small amount of water even at a lower temperature [82].

Beyond this, another role of water in the melting processes is that it affects the melting reaction and the chemical composition of the melt. During the dehydration melting process, all water involved is derived from hydrous minerals (Table 1). Dehydration melting reactions are incongruent reactions, and the melting produced is water-undersaturated. In contrast, the water-present melting reactions may be congruent, generally at low temperatures, or incongruent at high temperatures. When congruent melting occurs at low temperatures, the major minerals involved are quartz, K-feldspar, and plagioclase, all of which will melt together when no peritectic minerals are formed. In addition, depending on the mineral composition of the rocks, cordierite, sillimanite, mica, and amphibole can sometimes also be involved in the melting process. However, when water-present incongruent melting occurs at higher temperatures, the difference from congruent melting is the formation of typical peritectic minerals, such as amphibole, cordierite, garnet, or
aluminosilicates, all of which are newly formed minerals that do not exist in the protolith or the compositions of which have been varied [54].

The melting reaction and volume of melt produced by a given protolith depend critically on the presence of an aqueous fluid phase. In this way, water can control the geochemistry of granitic melts so that the melt produced under water-present conditions has a notably different chemical composition compared with that formed from dehydration melting. Free water can not only reduce the solidus of melting rocks but also reduce the stability of feldspar and quartz more effectively [31,54,63], and there would be more plagioclase and quartz involved in melting reactions [69]. Therefore, the melt produced via water-assisted melting generally has higher CaO and Na$_2$O contents and lower K$_2$O content [31], resulting in the generation of An-Ab-rich, Or-poor magma that prefers to concentrate in the An-Ab endmember on the An-Ab-Or ternary graph [54], which thus exhibits more tonalitic to trondhjemitic components.

As the water content increases, the MgO and FeO contents of the melt will also increase; thus, the composition of the melt is more likely to be mafic-rich [31]. The Al$_2$O$_3$ content in melt is mainly controlled by Al solubility, and excess Al will form peritectic phases, such as sillimanite [54]. Water could also increase the Al$_2$O$_3$ content in melt and then increase the aluminum saturation index (A/CNK) of melt, which is also the reason why most water-present melting experiments have higher A/CNK values in melt than those that are associated with the dehydration melting of hydrous minerals [31,97].

More importantly, the P-T path of the solidus curve for dehydration melting has a mostly positive slope, while the P-T path of the solidus curve for water-present melting is less sensitive to pressure (Figure 1). In the melting process of crust, dehydration melting leads to a volume increase in the entire system and in turn increases the system pressure, which deviates from the solidus curve and inhibits further melting, unless the pressure exceeds the rock toughness and subsequently causes brittle fracturing and melting separation.

The volume reduction in the system resulting from water-present melting benefits from the pressure-insensitive solidus curve, which does not easily affect the melting process. Moreover, the pressure gradient driven by the difference between low and high pressures will also absorb fluids and melts from the surrounding environment, resulting in the rapid accumulation of melt from local areas to form a large-volume melt, which is easier to separate from the sources and gather into a large-scale granitic magma chamber [51,54].

4. Effect of Dissolved Components in Fluids

Fluids usually contain large quantities of salts and volatile components [86–90,98], which not only have significant influences on crustal melting but are also closely associated with rare metal mineralization.

Most obviously, the existence of volatiles will significantly affect the solidus of granitic systems (Figure 3). Wyllie and Tuttle (1964) demonstrated that the addition of 5 wt.% dissolved components to water will observably lower the solidus of granite more effectively than pure water [40]. For example, P$_2$O$_5$ can reduce the solidus temperature by 20 °C, LiO$_2$ can decrease the temperature by 90 °C, and HF results in a 60 °C decrease. Manning (1981) discovered that fluids with 4 wt.% HF could decrease the solidus temperature by 100 °C in a simple granite system [99]. Moreover, Pichavant (1981) found that adding fluids containing 5 wt.% B$_2$O$_3$ to a Qz-Or-Ab system could decrease the solidus temperature by 60 °C, and even the solidus would decrease by 130 °C when the B$_2$O$_3$ content approached 17 wt.% [60]. However, Aranovich et al. (2013) concluded that high concentrations of brine exhibited a reduction in water activity, meaning the promotion effect on melting may not be as obvious as that in a simple pure-water system [55]. Winkler and Platen (1958) discovered that after the addition of NaCl solutions, cordierite gneiss began to generate granitic melt at 670 °C [100]. In a study regarding the melting of biotite–amphibole gneiss, Safonov et al. (2014) also found that NaCl solutions facilitated melting, but KCl brine produced a certain degree of melt suppression [62].
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In addition to the influence on the melting processes, fluid-assisted melting could facilitate the formation of specific granites. Acosta-Vigil et al. (2001) postulated that the melting of boron-rich, tourmaline-bearing metasedimentary rocks or melting assisted by boron-rich fluids may explain the formation of some leucogranites [101]. They pointed out that under a granitic wet solidus, B-rich fluid that flows through rocks rich in quartz and feldspar could effectively facilitate melting, thereby forming B-rich leucogranites. Li et al. (2003) and Wise et al. (2012) investigated the melting instigated by F-rich fluids, and fluorine was further enriched in granitic melt during crystallization differentiation, thereby forming F-rich granites, which is in agreement with the recognition that fluorine has a high partition coefficient between the granitic melts and most mineral phases [102,103]. Aranovich (2013, 2017) and Safonov et al. (2014) corroborated the ability of brine (including NaCl-KCl) to depress the solidus temperature of rocks and inhibit the dehydration of hydrous minerals [55,59,62]. They also noted that brine also promoted the break-down of feldspar and significantly increased the K_2O content of the melt, thereby forming potassium-rich granites. In a study regarding the melting of biotite–amphibole gneiss, Safonov et al. (2014) discovered that increased concentrations of KCl and NaCl facilitated amphibole depletion and conversion from orthopyroxene to clinopyroxene. As the brine concentration increased, the resultant melt composition became closer to the anhydrous (A-type) granite. Wang (2016) also suggested that brine-assisted anatexis could be a new pattern of post-orogenic A-type granites genesis [104].

Furthermore, during magma ascent, the water activity in brine will increase due to the reduction in pressure, which will greatly facilitate the melting of host rocks and will be beneficial to magmatic uprising. Moreover, some studies found that the metamorphic effect of brine increased the contents of alkali, CaO, and SiO_2 in the middle crust, making the host rocks of the middle crust more susceptible to anatexis [44,58].

![Figure 3. Effect of volatiles on the granite's wet solidus curve, modified from refs [40,41,60,99].](image-url)
Variations in the salt concentration in fluids can also influence the composition of the resultant magma. Safonov and Kosova (2017) found that changes in granitic composition can occur due to variations in the concentrations or compositions of salt (NaCl and KCl) in fluids [61]. As the NaCl and KCl concentrations increased, the A/CNK value of the melts decreased accordingly, even turning into mafic melts when the A/CNK value was below 1. Even if the concentrations of the salts were low, the changes in the composition of granitoids were extremely obvious [61]. In addition, what is noteworthy is that the concentrations used in these experiments were also typical concentrations for crustal fluids, which made the results of the study more realistic when deciphering the effect of natural fluids during the partial melting of crustal rocks.

Fluids containing dissolved components can affect the distributions of trace elements in the partial melting processes. Manning and Aranovich (2014) believed that brine has a higher capacity to extract light rare earth elements (LREEs) than heavy rare earth elements (HREEs) during the partial melting of crustal rocks [38]. This affects the distribution and fractionation of rare earth elements between melt and protolith, forming the melt with a higher LREE/HREE ratio. This was also confirmed by the experiment conducted by Li and Hermann (2017) [105]. Wang (2017) believed that the flux of brine is more conducive to the formation of mineralized granitoids, because halogen-rich, high-SiO$_2$ granitic magma derived by partial melting is similar to the hard-acid system owing to higher chemical hardness and electrophilicity, due to which, it is easier to extract these hard-base metal elements, such as W, Sn, REEs, and other metals, thus forming typical rare-metal granitoids in South China [106]. Li and Hermann (2017) found that chloride also promoted the incorporation of elements (e.g., Zn, V, and Pb) into melt [105]. It is generally accepted that the effect of Cl on trace element distribution is depolymerization on the melt structure induced by Cl or the complexing of Cl with trace elements. In water–rock reaction experiments, the presence of NaCl in fluids increased the solubility of REEs, especially for LREEs [65]. Similarly, in solubility experiments on apatite, Mair et al. (2017) and Tropper et al. (2011) found that NaCl and KCl have stronger selectivity for LREEs [107,108]. However, Cl-bearing fluids might have a negative influence on the release of trace elements into melt. On account of Cl-OH exchange, Cl-bearing fluids usually improve the stability of hydrous minerals (e.g., biotite and muscovite) by way of stronger Fe-Cl bonds [109]. To a certain extent, the stabilities of these minerals will hinder the incorporation of some rare metal elements into melt to a certain extent, as micas are important enrichment carriers of many rare metal elements in the crust.

Unlike chlorine, the presence of fluorine in fluids markedly increases the solubility of HREEs during the partial melting process [65,110]. Tropper et al. (2013) demonstrated that the increase in apatite solubility in NaF-bearing fluid was more significant than in NaCl-bearing fluid, and within the same concentration, the solubility of REEs in NaF-bearing fluid was 10 times higher than in NaCl-bearing fluid [110]. Beard et al. (2020) noted that the increase in F content not only facilitated REE release into the melt, but it also promoted the enrichment of other high-charge elements such as Zr, Hf, U, and Th in the melt [111]. Furthermore, Aseri et al. (2015) and Keppler (1993) found that the F content of magma significantly influenced the solubility of high-strength field elements (HSFEs), such as Zr, Hf, and Ti, and was more conducive for them to enter into highly evolved granitic melts [112,113]. However, the concentrations of large ion lithophile elements (LILEs) in melt, such as Li, Rb, Sr, and Ba, are limited by the F content [111]. This difference may be attributed to the ability of these metals to form stable complexes with F, which helps them dissolve and enter the melt/fluid phase [22,45,98,114]. In contrast, given that F-OH exchange widely exists in hydrous minerals, especially in biotite, where fluorine uptake will probably decrease the release of some rare metal elements into melts, fluorine in biotite causes a smaller separation between crystal layers and further improves mineral stability, which is similar to the effect of pressure [109].

Fluids containing CO$_3^{2-}$ and SO$_4^{2-}$ have also been observed to cause a more significant increase in the solubility of REEs in water–rock systems than pure water [65].

Fluids containing dissolved components can affect the distributions of trace elements in the partial melting processes. Manning and Aranovich (2014) believed that brine has a higher capacity to extract light rare earth elements (LREEs) than heavy rare earth elements (HREEs) during the partial melting of crustal rocks [38]. This affects the distribution and fractionation of rare earth elements between melt and protolith, forming the melt with a higher LREE/HREE ratio. This was also confirmed by the experiment conducted by Li and Hermann (2017) [105]. Wang (2017) believed that the flux of brine is more conducive to the formation of mineralized granitoids, because halogen-rich, high-SiO$_2$ granitic magma derived by partial melting is similar to the hard-acid system owing to higher chemical hardness and electrophilicity, due to which, it is easier to extract these hard-base metal elements, such as W, Sn, REEs, and other metals, thus forming typical rare-metal granitoids in South China [106]. Li and Hermann (2017) found that chloride also promoted the incorporation of elements (e.g., Zn, V, and Pb) into melt [105]. It is generally accepted that the effect of Cl on trace element distribution is depolymerization on the melt structure induced by Cl or the complexing of Cl with trace elements. In water–rock reaction experiments, the presence of NaCl in fluids increased the solubility of REEs, especially for LREEs [65]. Similarly, in solubility experiments on apatite, Mair et al. (2017) and Tropper et al. (2011) found that NaCl and KCl have stronger selectivity for LREEs [107,108]. However, Cl-bearing fluids might have a negative influence on the release of trace elements into melt. On account of Cl-OH exchange, Cl-bearing fluids usually improve the stability of hydrous minerals (e.g., biotite and muscovite) by way of stronger Fe-Cl bonds [109]. To a certain extent, the stabilities of these minerals will hinder the incorporation of some rare metal elements into melt to a certain extent, as micas are important enrichment carriers of many rare metal elements in the crust.

Unlike chlorine, the presence of fluorine in fluids markedly increases the solubility of HREEs during the partial melting process [65,110]. Tropper et al. (2013) demonstrated that the increase in apatite solubility in NaF-bearing fluid was more significant than in NaCl-bearing fluid, and within the same concentration, the solubility of REEs in NaF-bearing fluid was 10 times higher than in NaCl-bearing fluid [110]. Beard et al. (2020) noted that the increase in F content not only facilitated REE release into the melt, but it also promoted the enrichment of other high-charge elements such as Zr, Hf, U, and Th in the melt [111]. Furthermore, Aseri et al. (2015) and Keppler (1993) found that the F content of magma significantly influenced the solubility of high-strength field elements (HSFEs), such as Zr, Hf, and Ti, and was more conducive for them to enter into highly evolved granitic melts [112,113]. However, the concentrations of large ion lithophile elements (LILEs) in melt, such as Li, Rb, Sr, and Ba, are limited by the F content [111]. This difference may be attributed to the ability of these metals to form stable complexes with F, which helps them dissolve and enter the melt/fluid phase [22,45,98,114]. In contrast, given that F-OH exchange widely exists in hydrous minerals, especially in biotite, where fluorine uptake will probably decrease the release of some rare metal elements into melts, fluorine in biotite causes a smaller separation between crystal layers and further improves mineral stability, which is similar to the effect of pressure [109].

Fluids containing CO$_3^{2-}$ and SO$_4^{2-}$ have also been observed to cause a more significant increase in the solubility of REEs in water–rock systems than pure water [65].
Although fewer studies have concentrated on the roles of CO$_3^{2−}$ and SO$_4^{2−}$ in partial melting processes, carbonate and sulfate would also be essential complexation agents in enhancing the mobilities of rare earth elements during partial melting processes [115,116]. Regarding the influence of phosphorus, Garcia-Arias et al. (2012) partially melted two similar gneiss samples under identical experimental conditions and produced two melts with almost the same major elements but extremely different trace elements (e.g., REEs) [117]. The discrepancy was attributed to the P differences in the two melts, which obviously affected the solubility of apatite and monazite and indirectly inhibited the release of REEs into melt. Similarly, fluids containing P are likely to have similar effects on influencing the partitioning of trace elements during partial melting.

5. Challenges and Prospects

In the early stage, the research regarding the partial melting of crustal rocks and the genesis of granitoids focused on dehydration melting, and later, the model of fluid-present melting was focused on. Comparatively, fluid-present melting could contribute more to the diversity of granitoids and their mineralization. The majority of fluids used in fluid-present melting experiments mainly involve H$_2$O-CO$_2$ and KCl-NaCl-H$_2$O systems. However, there is still lack of research on other fluids, such as F-rich, B-rich, P-rich, and other complex volatile-bearing fluids. More importantly, most experiments have mainly focused on the changes in mineral facies and major element compositions, but fewer investigations have focused on trace elements due to the difficulty separating melts and mineral phases. With the development of in situ analysis and simulation techniques, LA-ICP-MS and the diamond-trap method could be used to separate melts from residue phases and achieve the analysis of trace elements in melts [28,117]. To better understand the role of fluids in partial melting, researchers must determine the mechanism of how fluid affects the distribution behavior of trace elements between minerals and melts, and more complex fluid compositions similar to natural fluids should be chosen to simulate these melting processes. This will facilitate a more comprehensive understanding of the melting of the Earth’s crust and provide strong theoretical constraints on the genesis of granitoids, the mineralization of granitoids, and the formation and evolution of the continental crust.

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References

1. Rudnick, R.L.; Gao, S. Composition of the Continental Crust; Treatise on Geochemistry; Elsevier Ltd.: Amsterdam, The Netherlands, 2004; pp. 1–64.
2. Rudnick, R.L. Making continental crust. Nature 1995, 378, 571–578. [CrossRef]
3. Sun, W.D.; Ling, M.X.; Yang, X.Y.; Fan, W.M.; Ding, X.; Liang, H.Y. Ridge subduction and porphyry copper-gold mineralization: An overview. Sci. China-Earth Sci. 2010, 10, 475–484. [CrossRef]
4. Sun, S.J.; Yang, X.Y.; Wang, G.J.; Sun, W.D.; Zhang, H.Z.; Li, C.Y.; Ding, X. In situ elemental and Sr-O isotopic studies on apatite from the Xu-Huai intrusion at the southern margin of the North China Craton: Implications for petrogenesis and metallogeny. Chem. Geol. 2019, 510, 200–214. [CrossRef]
5. Mao, J.W.; Cheng, Y.B.; Chen, M.H.; Franco, P. Major types and time–space distribution of Mesozoic ore deposits in South China and their geodynamic settings. Miner. Depos. 2013, 48, 267–294. [CrossRef]
6. Ballouard, C.; Massuyeau, M.; Elburg, M.A.; Tappe, S.; Viljoen, F.; Brandenburg, J.T. The magmatic and magmatic-hydrothermal evolution of felsic igneous rocks as seen through Nb-Ta geochemical fractionation, with implications for the origins of rare-metal mineralizations. Earth-Sci. Rev. 2020, 203, 103115. [CrossRef]
7. Wang, T.; Wang, X.X.; Guo, L.; Zhang, L.; Tong, Y. Granitoid and tectonics. Acta Petrol. Sin. 2017, 33, 1459–1478. (In Chinese)
70. Vielzeuf, D.; Holloway, J.R. Experimental determination of the fluid-absent melting relations in the pelitic system: Consequences for crustal differentiation. *Contrib. Mineral. Petrol.* **1988**, *88*, 257–276. [CrossRef]
71. Conrad, W.K.; Nicholls, I.A.; Wall, V.J. Water-saturated and -undersaturated melting of metaluminous and peraluminous crustal compositions at 10 kb: Evidence for the origin of silicic magmas in the Taupo volcanic zone, New Zealand, and Other occurrences. *J. Petrol.* **1988**, *29*, 765–803. [CrossRef]
72. Beard, J.S.; Lofgren, G.E. Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1, 3, and 6.9 kb. *J. Petrol.* **1991**, *32*, 365–401. [CrossRef]
73. Wolf, M.B.; Wyllie, P.J. Dehydration-melting of amphibolite at 10 kbar: The effects of temperature and time. *Contrib. Mineral. Petrol.* **1994**, *115*, 369–383. [CrossRef]
74. Zhou, W.G.; Xie, H.S.; Liu, Y.G.; Zheng, X.G.; Zhao, Z.D.; Zhou, H. Dehydration melting of solid amphibolite at 2.0 GPa: Effects of temperature and pressures. *Acta Geol. Sin.* **1995**, *69*, 326–336. (In Chinese)
75. Dyck, B.; Waters, D.J.; St-Onge, M.R.; Searle, M.P. Muscovite dehydration melting: Reaction mechanisms, microstructures, and implications for anatexis. *J. Metamorph. Geol.* **2020**, *38*, 29–52. [CrossRef]
76. Chen, G.N.; Grapes, R. *Granite Genesis: In-Situ Melting and Crustal Evolution*; Springer: Berlin/Heidelberg, Germany, 2009.
77. Wei, C.J. Granulite facies metamorphism and petrogenesis of granite (II): Quantitative modeling of the HT-UHT phase equilibria for metapelites and the petrogenesis of S-type granite. *Acta Petrol. Sin.* **2016**, *588*, 1611–1624. (In Chinese)
78. Burnham, C.W. Water and metasomatism: a mixing model. *Geochem. Cosmochim. Acta* **1975**, *39*, 1077–1084. [CrossRef]
79. Holmes, D.; Clemen, J.D.; Trello, P.J. Archean TTGs as sources of younger granitic magmas: Melting of sodic metatonalites at 0.6–1.2 GPa. *Contrib. Mineral. Petrol.* **2007**, *154*, 91–110. [CrossRef]
80. Droop, G.T.R.; Brodie, K.H. Anatectic melt volumes in the thermal aureole of the Etive Complex, Scotland: The roles of fluid-present and fluid-absent melting. *J. Metamorph. Geol.* **2012**, *30*, 843–864. [CrossRef]
81. Holtz, F.; Johannes, W. Genesis of peraluminous granites I. experimental investigation of melt compositions at 3 and 5 kb and various H2O activities. *J. Petrol.* **1991**, *32*, 935–958. [CrossRef]
82. Stevens, G.; Clemen, J.D.; Droop, G.T.R. Melt production during granulite-facies anatexis: Experimental data from “primitive” metasedimentary protoliths. *Contrib. Mineral. Petrol.* **1997**, *128*, 352–370. [CrossRef]
83. Hacker, B.R.; Liou, J.G. Influence of fluid and deformation on metamorphism of the deep crust and consequences for the geodynamics of collision zones. *Petrol. Struct. Geol.* **1998**, *10*, 297–323. [CrossRef]
84. Markl, G.; Bucher, K. Composition of fluids in the lower crust inferred from metamorphic salt in lower crustal rocks. *Nature* **1998**, *391*, 781–783. [CrossRef]
85. Audétat, A.; Gunther, D.; Heinrich, C.A. Formation of a magmatic-hydrothermal ore deposit: Insights with LA-ICP-MS analysis of fluid inclusions. *Science* **1998**, *279*, 2091–2094. [CrossRef] [PubMed]
86. Barnes, H.L. Hydrothermal processes: The development of geochemical concepts in the latter half of the twentieth century. *Geochim. Cosmochim. Acta* **1998**, *62*, 1611–1624. [CrossRef]
87. Dyck, B.; Waters, D.J.; St-Onge, M.R.; Searle, M.P. Muscovite dehydration melting: Reaction mechanisms, microstructures, and implications for anatexis. *J. Metamorph. Geol.* **2020**, *38*, 29–52. [CrossRef]
88. Newton, R.C. Fluid and shear zones in the deep crust. *World Geol.* **1990**, *182*, 21–37. [CrossRef]
89. Li, Z.L.; Yang, R.Y.; Sun, X.M.; Li, Y.S. Formation, evolution and mineralization of fluid during geological process. *Earth Sci. Front.* **1996**, *3*, 237–244. (In Chinese)
90. Yan, H.B.; Di, J.; Li, J.H.; Liu, Z.Y.; Liu, J.F.; Ding, X. Synthesis of zirconia micro-nanoflakes with highly exposed (001) facets and their crystal growth. *Crystals* **2021**, *11*, 871. [CrossRef]
91. Johannes, W.; Holtz, F. Formation and ascent of granitic magmas. *Geol. Rundsch.* **1991**, *80*, 225–231. [CrossRef]
92. Grant, T.B.; Harlov, D.E. The influence of NaCl-H2O fluids on reactions between olivine and plagioclase: An experimental study at 0.8 GPa and 800–900 degrees C. *Lithos* **2018**, *323*, 78–90. [CrossRef]
93. Ebadi, A.; Johannes, W. Beginning of melting and composition of 1st melts in the system Qz-Ab-Or-H2O-CO2. *Contrib. Mineral. Petrol.* **1991**, *106*, 286–295. [CrossRef]
94. Xu, Q.D. Fluid-absent melting experiment and modeling of crustal rocks: Major results and implication for study of granitoids. *Adv. Earth Sci.* **1997**, *12*, 35–42. (In Chinese)
95. Acosta-Vigil, A.; London, D.; Morgan, G.B.; Dewers, T.A. Solubility of excess alumina in hydrous granitic melts in equilibrium with peraluminous minerals at 700–800 degrees C and 200 MPa, and applications of the aluminum saturation index. *Contrib. Mineral. Petrol.* **2003**, *146*, 100–119. [CrossRef]
96. Ding, X.; Harlov, D.E.; Chen, B.; Sun, W.D. Fluids, metals, and mineral/ore deposits. *Geofluids* **2018**, *2018*, 1452409. [CrossRef]
97. Mann, D.A.C. An experimental study of the effect of fluorine on the crystallization of granitic melts. *J. Geol. Soc.* **1981**, *138*, 213–214.
98. Winkler, H.G.F.; Platen, H.V. Experimentelle gesteinsmetamorphose—II: Bildung von anatektischen granitischen schmelzen bei der metamorphose von NaCl-führenden kalkfreien Tonen. *Geochim. Cosmochim. Acta* **1958**, *15*, 91–112. [CrossRef]
99. Acosta-Vigil, A.; Pereira, M.D.; Shaw, D.M.; London, D. Contrasting behaviour of boron during crustal anatexis. *Lithos* **2001**, *56*, 15–31. [CrossRef]
102. Li, F.C.; Zhu, J.C.; Rao, B.; Jin, Z.D. Genesis of Li-F-rich granites: Experimental evidence from high temperature and high pressure. *Sci. China Ser. D-Earth Sci.* **2003**, *33*, 841–851.

103. Wise, M.A.; Francis, C.A.; Cerny, P. Compositional and structural variations in columbite-group minerals from granitic pegmatites of the Brunswick and Oxford fields, Maine: Differential trends in F-poor and F-rich environments. *Can. Mineral.* **2012**, *50*, 1515–1530. [CrossRef]

104. Wang, Y. Brine-assisted anatexis: A new model of post-orogenic A-type granites genesis. In Proceedings of the 2016th Annual Meeting of Chinese Geoscience Union, Beijing, China, 15 October 2016; p. 3. (In Chinese)

105. Li, H.J.; Hermann, J. The effect of fluorine and chlorine on trace element partitioning between apatite and sediment melt at subduction zone conditions. *Chem. Geol.* **2017**, *473*, 55–73. [CrossRef]

106. Wang, Y. Genesis of brine-induced melting of rare element granites in South China. In Proceedings of the 8th National Symposium on Metallogenic Theory and Prospecting Methods, Nanchang, China, 9 December 2017; pp. 243–244. (In Chinese).

107. Tropper, P.; Manning, C.E.; Harlov, D.E. Solubility of CePO$_4$ monazite and YPO$_4$ xenotime in H$_2$O and H$_2$O-NaCl at 800 degrees C and 1 GPa: Implications for REE and Y transport during high-grade metamorphism. *Chem. Geol.* **2011**, *282*, 58–66. [CrossRef]

108. Mair, P.; Tropper, P.; Harlov, D.E.; Manning, C.E. The solubility of CePO$_4$ monazite and YPO$_4$ xenotime in KCl-H$_2$O fluids at 800 degrees C and 1.0 GPa: Implications for REE transport in high-grade crustal fluids. *Am. Mineral.* **2017**, *102*, 2457–2466. [CrossRef]

109. Finch, E.G.; Tomkins, A.G. Fluorine and chlorine behaviour during progressive dehydration melting: Consequences for granite geochemistry and metallogeny. *J. Metamorph. Geol.* **2017**, *35*, 739–757. [CrossRef]

110. Tropper, P.; Manning, C.E.; Harlov, D.E. Experimental determination of CePO$_4$ and YPO$_4$ solubilities in H$_2$O-NaF at 800 degrees C and 1 GPa: Implications for rare earth element transport in high-grade metamorphic fluids. *Geofluids* **2013**, *13*, 372–380. [CrossRef]

111. Beard, C.D.; van Hinsberg, V.; Stix, J.; Wilke, M. The effect of fluorine on clinopyroxene/melt trace-element partitioning. *Contrib. Mineral. Petrol.* **2020**, *175*, 44. [CrossRef]

112. Aseri, A.A.; Linnen, R.L.; Che, X.D.; Thibault, Y.; Holtz, F. Effects of fluorine on the solubilities of Nb, Ta, Zr and Hf minerals in highly fluxed water-saturated haplogranitic melts. *Ore Geol. Rev.* **2015**, *64*, 736–746. [CrossRef]

113. Keppler, H. Influence of fluorine on the enrichment of high field strength trace elements in granitic rocks. *Contrib. Mineral. Petrol.* **1993**, *114*, 479–488. [CrossRef]

114. Yan, H.B.; He, J.J.; Liu, X.W.; Wang, H.B.; Liu, J.F.; Ding, X. Thermodynamic investigation of the hydrolysis behavior of fluorozirconate complexes at 423.15–773.15 K and 100 MPa. *J. Solut. Chem.* **2020**, *49*, 836–848. [CrossRef]

115. Louvel, M.; Etschmann, B.; Guan, Q.S.; Testemale, D.; Brugger, J. Carbonate complexation enhances hydrothermal transport of rare earth elements in alkaline fluids. *Nat. Commun.* **2022**, *13*, 1456. [CrossRef]

116. Zheng, X.; Liu, Y.; Zhang, L. The role of sulfate-, alkali-, and halogen-rich fluids in mobilization and mineralization of rare earth elements: Insights from bulk fluid compositions in the Manning-Dechang carbonatite-related REE belt, southwestern China. *Lithos* **2021**, *386*, 106008. [CrossRef]

117. Garcia-Arias, M.; Guillermo Corretge, L.; Castro, A. Trace element behavior during partial melting of Iberian orthogneisses: An experimental study. *Chem. Geol.* **2012**, *292*, 1–17. [CrossRef]