A revisit to phase transition behavior of K-feldspar at high-pressure and high-temperature: Implications on metastable K-feldspar in cold subduction

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Abstract

Felsic gneiss is main type of ultrahigh-pressure metamorphic rocks in continental subduction zones. As one of the important mineral of felsic gneiss, the phase behavior of K-feldspar is of great significant to study subducting seismic activities, crust-mantle interactions and plate tectonics in the Earth's interior. Thus, the phase relations in K-feldspar are constrained by Raman spectroscopy combined with externally-heating diamond anvil cell (DAC) under high-pressure (28 GPa), high-temperature (400 °C), and simultaneous high pressure-temperature (P-T) (14 GPa, 430 °C) conditions. The phase diagram of K-feldspar at relatively lower temperature has been complemented, and a more comprehensive P-T phase diagram of K-feldspar is established along with previous results. K-feldspar undergoes a reversible phase transition from C-1 to P-1 (metastable K-feldspar) symmetry at 10.3 GPa. Metastable K-feldspar is an intermediate phase from K-feldspar to K-holl-I (KAlSi3O8 with a hollandite-I structure) in extremely cold subduction slabs (<2°C/km) or the center of some old, cold, and rapidly subducting slabs. Metastable K-feldspar is stable even at 11.4 GPa and 400°C in enriched hydroxyl group (OH) environments, which shows greater high P-T stability than K-feldspar. So metastable K-feldspar could withstand subduction-zone fluids low-temperature metamorphism and survive to deeper than previously expected. This study enhances our understanding of the formation paths and conditions of K-holl-I, the subducted depth of K-feldspar, the effect of subduction-zone fluids on continental subduction, and provides a possible reason for the origin of intermediate- and deep-focused seismicity.
Keywords: metastable K-feldspar, Raman spectroscopy, high pressure-temperature conditions, continental subduction, subduction-zone fluids
Introduction

Feldspar minerals comprise about 50-60% of the Earth’s crust and are widely found in the surface of other planets (e.g., Moon, Mars, Venus) (Sprague et al. 1997; Rogers and Nekvasil 2015; Hashimoto et al. 2009). K-feldspar (microcline, sanidine, orthoclase; KAlSi$_3$O$_8$) is more stable than other two principal rock-forming end-members (albite, anorthite), and has been regarded as a predominant potassic phase in the Earth’s crust and the uppermost mantle (e.g., Liu et al. 2010; Deng et al. 2011). In addition, K-feldspar could enter the deep Earth via subduction process, crustal constituents are directly transferred from the descending slab into the mantle wedge at different depths, leading to the crust-mantle interaction (Irifune et al. 1994; Zhang et al. 2003; Zheng 2012). Furthermore, K-holl-I is regarded as a host phase for large cations such as K, Na, Sr, Ba, and Pb in the mantle, which is of great geochemical interest (e.g., Yamada et al. 1984). Thus, the stability of K-feldspar is of great geophysical and geochemical significance to understand the dynamics of subducting lithospheres, Earth’s long-term thermal evolution, and the material exchange of the crust-mantle system.

The framework of K-feldspar is based on the rings of four TO$_4$ tetrahedra (T = Si$^{4+}$, Al$^{3+}$) forming double crankshaft-like chains. All Si and Al atoms are bonded to four O atoms in the TO$_4$ tetrahedra, and potassium atoms occupy the large voids. K-feldspar dives into the Earth interior along with a series of structural and compositional changes. Phase equilibrium experiments confirmed that at temperatures above 700 °C, K-feldspar dissociated into a denser assemblage of K$_2$Si$_4$O$_9$ wadeite +
kyanite + coesite/stishovite (Wd + Ky + Coe/St) at 6-7 GPa, and latter the assemblage recombined into K-holl-I at 9-10 GPa (e.g., Urakawa et al. 1994; Yagi et al. 1994; Liu et al. 2010). K-holl-I transformed into K-holl-II (KAlSi$_3$O$_8$ with a hollandite-II structure) at near 20 GPa, both ambient and elevated temperatures. K-holl-II is unquenchable and stable over the entire range of mantle conditions (Sueda et al. 2004; Nishiyama et al. 2005; Ferroir et al. 2006; Hirao et al. 2008); In addition, K-feldspar melted to leucite (KA1Si$_2$O$_6$) and silica-rich liquid at 2 GPa, 1150 °C (Lindsley 1966), and transformed into metastable phase induced by an increase in the Al coordination number at 10-13 GPa and ambient temperature (Pakhomova et al. 2020).

Metastability of subducted minerals could encourage subducting slabs deceleration or stagnation (e.g., Van Mierlo et al. 2013; Agrusta et al. 2014). It is well known that low-temperature parts in the Earth’s subduction zones enable the preservation of metastable phases at greater depths than those under equilibrium conditions (e.g., Hogrefe et al. 1994; Kawakatsu and Yoshioka 2011). However, previous high $P$-$T$ studies of K-feldspar are insufficient to be applied to in the ultracold subducted environments, and the lower temperature parts (below 700 °C) of the phase diagram has not be carefully investigated yet. Besides, Pakhomova et al. (2020) studied the stability of metastable albite and anorthite by quenching experiments, and proposed anorthite may exist at deeper depths than expected in the Earth's interior. As one of the important mineral of felsic gneiss, the high $P$-$T$ stability of metastable K-feldspar is also worthy of attention. Herein, the phase relations at relatively low temperature of K-feldspar are investigated firstly by Raman
spectroscopy in externally-heating DAC under high-pressure (28 GPa), high-temperature (400 °C), and simultaneous high $P-T$ (14 GPa, 430 °C) conditions. We also presented the isothermal ($\gamma_iT$) mode Grüneisen parameters, isobaric ($\gamma_iP$) mode Grüneisen parameters, and intrinsic anharmonic mode parameters of K-feldspar. Besides, a series of ex situ multi-anvil experiments were performed to clarify the high $P-T$ stability of metastable K-feldspar. This study complements the gap in the phase diagram of K-feldspar at relatively low temperature, and a more comprehensive $P-T$ phase diagram of K-feldspar is established along with previous studies. The results provide new insights into the phase behavior of K-feldspar in subduction zone at different thermal gradients (especially at the ultracold), and the possible seismicity caused by their intruding plates (Zheng 2019).

Material and Methods

Sample synthesis and characterization

High-purity K-feldspar was synthesized by solid-state reaction. Reagent-grade KHCO$_3$, Al$_2$O$_3$ and SiO$_2$ powders were mixed in a molar 2:1:6 ratio. The powder mixtures were crushed with ethanol in an agate mortar for 1 h, and then placed in a Pt crucible and heated up to 800 °C in a stove for 12 h to ensure a sufficient decarbonation. The recovered mixture was ground finely and then pressed into pellets with diameter of 6 mm and length of 3 mm under uniaxial pressure of 4 MPa. High $P-T$ synthesis experiment was performed on DS 6 × 600 t cubic-anvil-type apparatus at the Key Laboratory of High-Temperature and High-Pressure Study of the Earth's
Interior, Institute of Geochemistry, CAS, Guiyang, China. Figure 1 (a) shows a schematic of the cross section of the experimental assemblage. A pellet was covered by the silver foil of 0.025 mm thickness, pyrophyllite cube (32.5 mm × 32.5 mm × 32.5 mm) and h-BN were applied as the pressure medium, and a graphite was used as the heater at 1.8 GPa, 900 ℃ for 2 h. The pressure was reduced to ambient conditions after quenching. The reactant was confirmed as a K-feldspar single phase by both powder X-ray and Raman spectrum, as Figures 1 (b-c) shown.

In situ high-pressure and high-temperature Raman experiments

The Raman spectra of synthetic K-feldspar under high-pressure (up to 28 GPa) and room-temperature, high-temperature (up to 400 ℃) and ambient-pressure, and simultaneous high \( P-T \) conditions (up to 14 GPa, 430 ℃) were collected in DAC. The sample chambers were firstly compressed up to target pressures, and then heated. High-pressure conditions were generated by a pair of 400 mm diamond culets. The 250-μm-thick rhenium gaskets were pre-intended to dense disks of ~60 μm thickness, and then drilled a hole as the sample chamber with a diameter of ~160 μm. The 4:1 mixture of methanol-ethanol (ME), 16:3:1 mixture of methanol-ethanol-water (MEW), helium, nitrogen or ultrapure water (H₂O) were selected as pressure-transmitting mediums (PTMs). The gaseous PTMs were loaded by a high-pressure gas-loading apparatus sealed at above 0.4 GPa. The gas-loading apparatus is developed in the Sanchez Technologies and located at the Key Laboratory of High-Temperature and High-Pressure Study of the Earth's Interior, Institute of Geochemistry, CAS, Guiyang.
High-temperature environments were achieved by two external electric NiCr resistance heating furnace in series around the diamonds. Temperatures were measured by a R/S type platinum–rhodium and platinum thermocouple (Omega technology company, America) with the precision of ±1 °C in our experimental temperature range. The thermocouple was used for temperature measurement and stabilization through a feedback loop in the temperature controller (CN3251, Omega technology company). Every time before the Raman spectrum was collected, we kept the temperature at least 5 min to guarantee the stabilization and uniformity of temperature in the sample chamber. The R1 line of tiny ruby (Cr$^{3+}$ doped α-Al$_2$O$_3$) spheres and 0-0 line of SrB$_4$O$_7$:Sm$^{2+}$ grains (synthetic method was described in previous study) (Mao et al. 1986; Zhao et al. 2017) were selected to calibrate pressure at high-pressure and high $P$-$T$ experiments, respectively. Compared to Ruby, the 0-0 line of SrB$_4$O$_7$:Sm$^{2+}$ presents very small temperature response, including frequency shift and broadening. So it is the preferred pressure calibration under high $P$-$T$ conditions. The spectra of the calibrator were measured at each pressure before and after sample data collection, and the average pressure values were taken. The Raman spectra were collected at a confocal Renishaw in Via Raman Microscope in the Key Laboratory of High-Temperature and High-Pressure Laboratory Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The tilting and rotation of the spectrometer relative to the incident laser beam were calibrated using a silicon wafer with a static spectrum centered at 520 cm$^{-1}$. Samples were excited by an Argon ion laser ($\lambda = 514.5$ nm) operated at 20 mW with a focused laser spot of ~5 μm in
diameter through a SLM Plan 50 × Olympus microscope objective. A spectrometer
with a liquid nitrogen-cooled CCD detector was used to collect the Raman data. The
accurate peak positions of the Raman spectra were fitted by PeakFit software.

Multi-anvil experiments

The high P-T conditions of quenching experiments were provided using a
1000-ton Kawai-type multi-anvil apparatus at the Key Laboratory of
High-Temperature and High-Pressure Study of the Earth’s Interior, Institute of
Geochemistry, CAS, Guiyang, China. The sample assembly was displayed in Figure
S1. Eight tungsten carbide cubes with a truncation of 6 mm were used as second-stage
anvils, and a Cr2O3-doped MgO octahedron with edges of length of 14 mm was used
as pressure medium. Starting materials were the high-purity K-feldspar synthesized in
this study. Graphite sleeve, platinum closure column, MgO tube, ZrO2 tube and Al2O3
plug were used as the heater, the sample capsule, the insulator, and the thermal
insulation sleeve, respectively. The temperature was measured using a
W95Re5-W74Re26 thermocouple inserted axially under the sample capsule. To remove
absorbed water, all parts composed of MgO, Al2O3, or ZrO2 were baked at 1000 °C
for 1 h before the experiments. The sample chambers of three quench experiments
were firstly compressed up to 15 GPa, and then heated to 500 °C, 650 °C, and 800 °C
at a rate of 20 °C/min, respectively. The duration time at each target temperature was
at least 2 h before rapid quenching.
Results and Discussion

Raman spectrum of K-feldspar at ambient conditions is presented in Figure 1 (b). 12 modes of the 39 Raman modes (20A_g + 19B_g) predicted by factor group analysis (Tseng et al. 1995) were observed. The strongest triplet peaks at 451.98, 475.44, and 512.98 cm^{-1} (denoted as I_a, I_b, I_c modes) are ascribed to the ring-breathing of the four-membered rings of tetrahedra. Three Raman peaks at 117.23, 156.34, and 195.19 cm^{-1} (expressed as III_a, III_b, III_c modes) are assigned to cage-shear. Two peaks at 282.91 and 403.21 cm^{-1} (named as II_a, II_b modes) are due to the rotation-translation of the four-membered rings. Two weak modes at 758.76, 803.59 cm^{-1} (marked as IV_a and IV_b modes) are attributed to the deformation of the tetrahedra. The broad peaks with position at around 1023.44 and 1118.38 cm^{-1} (labeled as V_a and V_b) belong to the vibrational stretching modes of the tetrahedra. Most Raman modes coincide well with previous studies, except for the modes of IV_a, IV_b, V_a and V_b due to the weak intensity (Freeman et al. 2008; Bendel and Schmidt 2008; Peterson et al. 2009; Befus et al. 2018). The slight differences in wavenumber for observed modes may result from the synthetic environment, peak overlap, and orientation dependence.

Raman spectroscopy of K-feldspar at high-pressure/high-temperature

High-pressure Raman spectra of K-feldspar were collected up to 28 GPa at room temperature, and were only studied in the spectral range 100-800 cm^{-1} due to the intense Raman bands of MEW at 880-1200 cm^{-1}. The typical high-pressure Raman spectra are showed in Figure 2 (a). At high pressure, a general deterioration of the
Raman signal and amorphization effect can be observed. \( I_b, I_c, II_a, III_b \) modes can be distinguished clearly within 10 GPa, while only the strongest mode \( I_c \) can be observed clearly within the entire studied pressure range. All the Raman modes shift to higher wavenumbers with increasing pressure because of the TO\(_4\) tetrahedra shrinkage and the stronger electrostatic repulsion. The corresponding pressure shifts and the full width at half maximum (FWHM) of \( I_c \) mode are plotted in Figures 2 (b-c), from which two obvious inflection points at 6.5 GPa and 14.7 GPa can be observed, and another obvious inflection point at 10.3 GPa can be seen in Figure 2 (c). The pressure coefficient (\( \partial \nu_i / \partial P \)) changes from 3.72(2) to 3.07(9) cm\(^{-1}\)GPa\(^{-1}\) at the first discontinuity point (at 6.5 GPa). However, X-ray diffraction (XRD) studies reported microcline experienced a continuous compression up to 7 GPa, then underwent an elastic softening with an increase of the \( a \)-axis and a decrease of the \( b \)-axis at 7-9 GPa; meanwhile, the \( \alpha \) and \( \beta \) unit-cell angles rapidly increased while the \( \gamma \) unit-cell angle decreased at pressures above 6.7 GPa (Allan and Angel 1997; Pakhomova et al. 2020). Thus, the first discontinuity point at 6.5 GPa could not be ascribed to a phase transition but the change in compressional mechanism at atomic scale, which result in the elastic behaviour change. Similar discontinuity was also found in the isostructural mineral, low albite, at 6.5 GPa (Aliatis et al. 2017). The wavenumbers of \( I_c \) mode change linearly upon further compression from 6.1 to 14.2 GPa, whereas the FWHM shows an abrupt change at \ (~10.3 GPa). Similar discontinuity was also found in low albite at 8.5 GPa with the \( \partial \nu_i / \partial P \) of the mode at 815 cm\(^{-1}\) (corresponding to \( IV_b \) modes) showing a discontinuity (Aliatis et al. 2017). Pakhomova et al. (2020) reported a
displacive phase transition of K-feldspar from C-1 to P-1 (metastable phase) symmetry, which was induced by an increase in the Al coordination number from four to six upon 10.4-12.8 GPa. Thus, we infer the second discontinuity at 10.3 GPa is relate to the phase transition from K-feldspar to metastable phase. The accurate phase transition range is 9.7 to 10.8 GPa. An additional Raman experiment up to 13 GPa demonstrated the reversibility of the phase transition (Figure S2 (a)). The third discontinuity at 14.7 GPa is relate to the solidification of MEW which caused an irreversible pressure-induced amorphization. The high-pressure behaviour of feldspars is highly sensitive to deviatoric stress. Previous study reported metastable K-feldspar was stable at least up to 27 GPa in hydrostatic conditions (Pakhomova et al. 2020). While in this study, the FWHM of $I_c$ mode increased and the intensity decreased rapidly at above 14.7 GPa. Upon further compression at above 23.1 GPa, sample was fully amorphous and remained amorphous structure on recovery to ambient conditions. Another high-pressure Raman experiment in H$_2$O up to 20.4 GPa indicated the reversibility of the not fully amorphization (Figure S2 (b)). Previous results about the pressure-induced phase transition of feldspars at room temperature reported a displacive phase transition occurred for both anorthite and oligoclase at 2.2-3.9 GPa, accompanied by the occurrence of a new peak near the $I_c$ mode, which was mainly caused by the reduction of Ca-O bond length (Xie et al. 2012; Pakhomova et al. 2020). However, the phase transition behavior was not found in K-feldspar and albite during the compressing processes (Aliatis et al. 2017; Pakhomova et al. 2020). We infer the phase behavior at relative low pressure of feldspars is significantly affected by the...
(Ca,Na,K)-O bond length and bond energy. Moreover, the three end-members all experienced a coordination number increase of Al atoms to further adapt to the high-pressure conditions (Pakhomova et al. 2020).

High-temperature Raman spectra of K-feldspar were collected up to 400 °C at ambient pressure. The typical high-temperature Raman spectra are showed in Figure 3 (a), and the variation of Raman shift at different temperatures is plotted in Figure 3 (b). The Raman shifts of all observed bands for K-feldspar continuously decrease with increasing temperature, and no phase transition was observed during heating in this study, which was consistent with previous studies (Henderson 1979; Hovis et al. 2010). Generally, the Raman peaks shift slightly to lower frequency regions with increasing temperature because of the longer bond length and weaker bond. Changes of FWHM and signal intensity of Raman peaks under high-temperature conditions are not great as that under high-pressure conditions (i.e., increase of FWHM is ~4.7 cm$^{-1}$ for $I_c$ mode in the investigated temperature range).

Combined the Raman spectra of K-feldspar under high-pressure and high-temperature conditions, the pressure coefficients ($\partial \nu_i/\partial P$) and the temperature coefficients ($\partial \nu_i/\partial T$) of observed Raman bands are listed in Table 1 and Figure S3. The Raman modes could be seen approximately as continuous increases within ~10.3 GPa. The pressure coefficients of Raman vibrations of K-feldspar vary from 1.41 to 5.32 cm$^{-1}$GPa$^{-1}$, and the temperature coefficients vary from $-0.17 \times 10^{-2}$ to $-0.82 \times 10^{-2}$ cm$^{-1}$K$^{-1}$. The modes relate to the rotations of the four non-equivalent tetrahedra and the translation of K$^+$ cations (e.g., $III_a$, $III_b$, Aliatis et al. 2015) show the biggest
change in slope with pressure and temperature. The isothermal \( \gamma_{iT} \) and isobaric \( \gamma_{iP} \) mode Grüneisen parameters are important physics quantities to describe the elasticity and anharmonicity under high \( P-T \) conditions, which can be calculated by the following equations and are listed in Table 1 (Gillet et al. 1989):

\[
\begin{align*}
\gamma_{iT} &= \left( \frac{K_T}{\nu_{i0}} \right) \left( \frac{\partial \nu_i}{\partial P} \right)_T \\
\gamma_{iP} &= -\left( \frac{1}{\nu_{i0}} \alpha \right) \left( \frac{\partial \nu_i}{\partial T} \right)_P
\end{align*}
\]

where \( \nu_i \) is the Raman shift of the \( i \)-th vibrational mode, \( \nu_{i0} \) is the frequency of mode \( \nu_i \) at 0 GPa, \( K_T \) is the isothermal bulk modulus with value of 58.3 GPa (Allan and Angel 1997), \( \alpha \) is the volume thermal expansion coefficient with value of \( 1.44 \times 10^{-5} \text{K}^{-1} \) (Henderson, 1979), defined as \( \alpha = (1/V) \left( \frac{\partial V}{\partial T} \right)_P \). The calculated values of \( \gamma_{iT} \) range from 0.26 to 1.96, and \( \gamma_{iP} \) change from 0.41 to 4.51. The average \( \gamma_{iT} \) value of Raman modes of tetrahedra (0.32) are much smaller than that of the tetrahedral cages (1.96), and the thermal expansion differs more with a smaller average \( \gamma_{iP} \) value of tetrahedra (0.61) and a larger average \( \gamma_{iP} \) value of the tetrahedral cages (3.42). The average \( \gamma_{iT} \) and \( \gamma_{iP} \) values are small for the TO₄ tetrahedra, which reflects their relative incompressibility and weak expansivity. Hence, the weaker bonds (K-O) are affected more by increasing pressure and temperature. It is obvious that the tetrahedra are much more incompressible than the tetrahedral cages, which is consistent with other feldspars (e.g., oligoclase from Xie et al. 2012). The \( \gamma_{iP} \) are different with the \( \gamma_{iT} \) for same mode, which means an intrinsic anharmonicity. The intrinsic anharmonic mode parameter \( \beta_i \) can be calculated by the following equation and are listed in Table 1:

\[
\beta_i = \alpha (\gamma_{iT} - \gamma_{iP})
\]

the obtained \( \beta_i \) change from \(-0.46 \times 10^5\) to \(-0.16 \times 10^5 \text{K}^{-1}\), with an average of \(-0.26 \times 10^5 \text{K}^{-1}\).
Raman spectroscopy of K-feldspar at simultaneous high $P$-$T$ conditions

Raman spectra of K-feldspar in different PTMs were collected at pressures up to 14.7 GPa and temperatures up to 430 °C (Figure S4). During heating at a certain initial pressure, the real pressure of sample chamber changed because of thermal expansion and stress relief of experimental materials. Thus, we measured the pressure of sample chamber by the fluorescence spectra of SrB$_4$O$_7$:Sm$^{2+}$ in real-time. The representative Raman spectra of K-feldspar obtained under simultaneous high $P$-$T$ conditions are presented in Figure 4. Given the 4:1 ME mixture can conveniently provide a hydrostatic condition at below 10.5 GPa (Klotz et al. 2009), and has relatively simple ingredients, it was firstly selected as the PTM. At first initial pressure points of 1.8 GPa, with temperature increasing, no any meaningful variation except pressure- and temperature-induced frequency shifts were observed (Figure S4 (a)). With further compressing and heating, the peak shape changed firstly at 400 °C and 5.9 GPa with a new peak appearing at $\sim$430 cm$^{-1}$, and the Raman shift of mode at $\sim$290 cm$^{-1}$ clearly showed a discontinuous evolution (Figure S4 (b)). Then the variation became apparent at 400 °C and 6.7 GPa with several new peaks at 206, 215, 357, 392, 430, and 465 cm$^{-1}$, while some new peaks disappeared after further heating (Figure S4 (c)). We even observed some bubbles welling up in the sample chamber, but it was hard to record and measure because of its quick breaking. Similar Raman spectra variation were also observed at $P$-$T$ range of 350-430 °C and 7.3-8.1 GPa (Figure S4 (d)), while surprisingly did not appear at 11.4-13.9 GPa (Figure S4 (e)).
The new peaks revealed at least one reaction occurred. Due to the signal-to-noise ratio deterioration and the Raman peaks broadening under high P-T environments, it was difficult to identify the new phase via the ambiguous peaks. Luckily, the new peaks sharpened and the shape of the main strong peaks remain unchanged during cooling and decompressing periods (Figure S5), which made the recovered sample easy to distinguish, and could be referred to the high P-T new phase. Raman spectra of samples recovered from high P-T to ambient conditions in different PTMs are shown in Figure 5. The Raman spectrum of recovered sample from 430 °C, 6.7 GPa (ME) in Figure 5 is virtually same as that in Figures S4 (b-d), and it is consistent well with the characteristic peaks of an assemblage of coesite, stishovite and KHCO₃ (Figure S6 (a)). Besides, we accidentally conducted another experiment at 4.7-5.9 GPa, 20-400 °C in the 16:3:1 MEW mixtures (Figure S4 (f)), and the Raman spectrum of recovered sample can be indexed to coesite and muscovite (Figure S6 (b)). However, because of the appearance of coesite, and the reaction did not occurred in the P-T range of 1.8-3.2, 11.4-13.9 GPa and 20-400 °C (Figures S4 (a) and S4 (c) ), it was difficult to confirm whether the ME/MEW mixtures reacted with K-feldspar or with its phase transition products, such as wadeite-type K₂Si₄O₉(Wd). In order to further study the stability of K-feldspar under high P-T conditions, we replaced the PTM. We conducted two high P-T experiments in helium and in no PTM, respectively (Figures S4 (g-h)), and found K-feldspar was stable at the experimental P-T range.

All up, pure K-feldspar is stable and does not decompose to an assemblage of Wd + Ky + Coe/St within the P-T range (0-11.4 GPa, 20-430 °C) in this study.
Nonetheless, if fluid components added, the stability of K-feldspar is different. The results of in situ Raman experiments under high $P$-$T$ conditions in ME/MEW show: K-feldspar (low Al coordination number) could be stable only below 4.5 GPa, 400 °C in ME/MEW fluids. Once exceeding this limit, it transforms into the assemblage containing coesite, then with pressure increasing, the transformation temperature gradually drops to 350 °C (8.1 GPa). The phase transition of K-feldspar to the assemblage containing coesite is irreversible and has negative Clapeyron slope. However, after the structural transition of K-feldspar into metastable structure (high Al coordination number) at above 10.3 GPa, metastable K-feldspar could remain stable even at 11.4 GPa and 400 °C, showing a higher structural stability. Subduction zone fluids greatly affect the mineral transformation, rock melting, element mobility, and water (H$_2$O) is an important fluid of subduction-zone rocks. For verifying whether the higher structural stability of metastable K-feldspar still remain in the deep Earth fluids, we conducted another two high $P$-$T$ Raman experiments using H$_2$O as the PTM. In H$_2$O, K-feldspar transformed into the assemblage containing coesite at 6.9 GPa and 350 °C (Figure S4 (i), Figure S6 (c)), while metastable K-feldspar could remain stable at up to 10.4 GPa and 430 °C (Figure S4 (j)), almost same as in ME/MEW. The decomposition of metastable K-feldspar into coesite mixture after keep in 430 °C for 1 h may be ascribed to the pressure change. The pressure of sample chamber decreased to 9.8 GPa because of thermal expansion and stress relief after 1 h, so the metastable phase transformed back to K-feldspar, then K-feldspar was not stable and decomposed. Therefore, metastable K-feldspar may be harder to undergo
metasomatism with subduction-zone fluids and can survive to deeper than previously expected. In addition, the coesite mixture remain stable at 430 °C, 9.8-10.4 GPa after 50 min (Figure S7), which indicates the decomposition of K-feldspar in fluid composition could occur at 4.5 GPa, 400 °C and maintained at a certain $P$-$T$ range before the transition from K-feldspar to metastable phase. It is hard to identify unambiguously the equilibrium phase(s) due to the kinetics of the phase transition. But the stable existence of coesite with pressure and temperature increasing indicate that the assemblage containing coesite is more stable than K-feldspar with low Al coordination number at above 4.5 GPa, 400 °C.

Pressure-temperature phase diagram of K-feldspar

The phase diagram of K-feldspar under high $P$-$T$ conditions constrained by experimental data is shown in Figure 6 along with the literature data (Lindsley 1966; Zhang et al. 1993; Urakawa et al. 1994; Yagi et al. 1994; Nishiyama et al. 2005; Akaogi et al. 2004; Ferroir et al. 2006; Yong et al. 2006; Hirao et al. 2008; Chen et al. 2019; Guo et al. 2020; Pakhomova et al. 2020). The black solid lines represent the phase boundaries determined by high $P$-$T$ experiments or from previous phase diagram, the dotted lines indicate the extrapolated phase boundaries by limited data. We make following changes comparing to previous studies of the phase relations of K-feldspar (Urakawa et al. 1994; Sueda et al. 2004; Nishiyama et al. 2005; Yong et al. 2006; Hirao et al. 2008; Liu et al. 2010): First of all, this study complements the blank of previous data under relatively low $P$-$T$ conditions, and get more accurate $P$-$T$ phase
boundaries between K-feldspar and Wd + Ky + Coe/St by Raman spectroscopy. Secondly, previous phase diagrams revealed that KAlSi3O8 with a hollandite-I and -II structures (K-holl) was stable under relatively high-pressure and low-temperature conditions. However, former studies referred to the experimental data of e.g., Nishiyama et al. (2005), in which they used K-holl-I as starting sample rather than K-feldspar. Since K-holl-I phase is quenchable, it can be detected under high-pressure, low-temperature and even ambient conditions. Combined high-pressure stability of K-feldspar in this study, the former data are not reasonable to interpret the phase behavior of K-feldspar at this $P$-$T$ area in which K-holl phase has not formed yet. To solve this problem, three quench experiments of K-feldspar in multi-anvil apparatus were performed at 15 GPa, 500 °C, 15 GPa, 650 °C, and 15 GPa, 800 °C, respectively. Raman analysis on the three quenching samples revealed the existence of K-feldspar, K-feldspar + K-holl-I, and K-holl-I (with all peaks indexed well to that in Chen et al. 2019), respectively (Figure 7). For sufficient phase equilibrium, the quench experiments at 15 GPa, 500 °C was kept for 12 h before rapid quenching, and the characterized result at 15 GPa, 500 °C indicates K-feldspar is a stable phase at below 15 GPa, 500 °C. The coexistence of K-feldspar and K-holl-I at 15 GPa, 650 °C shows metastable K-feldspar is the intermediate phase between K-feldspar and K-holl-I under relatively high-pressure and low-temperature conditions. Thus, on the basis of previous phase diagram, we re-predicted the phase boundary between K-feldspar and K-holl by the results of three quenching experiments in this study, and only reserved the data of Nishiyama et al. 2005 at above the phase boundary. Finally, the phase
boundary between K-holl-I and K-holl-II phase was re-constrained by the data of Hirao et al. (2008) in which they used K-feldspar as the starting sample.

Implications

The phase diagram of K-feldspar in the ultracold and dry subducting slab, as shown in Figure 8 (a), suggests that the pressure-induced phase transition of K-feldspar at relatively low-temperature (< 650 °C) could be different from those occurring at relatively high-temperature (> 650 °C). Instead of the K-feldspar→liquid / liquid + leucite in the normal or warmer mantle (> 5 °C/km), or K-feldspar→Ky + Wd + Coe/St in the ultracold subduction environments (~5 °C/km) (Zheng and Hermann 2014; Zheng 2019), K-feldspar firstly transforms into metastable phase at above 10.3 GPa at relatively low-temperature. The metastable phase transition could occur in extremely cold plates (~2 °C/km, like Tonga proposed by Syracuse et al. 2010) at depths of ~300 km. Additionally, because the slab center is much colder than the margin in some cold, old, fast, and steep slabs (Ranalli et al. 2000; Kubo et al. 2009; Xu et al. 2020), metastable feldspar is also likely to preserve within the center of some ultracold, old, and rapidly subducting slabs. The density is similar between metastable K-feldspar and the mantle at the phase transition depth (~300 km) (Pakhomova et al. 2020). Thus, metastable K-feldspar has possible influence on the dynamics of subducted continental lithosphere, that is, affects buoyancy, hampers further subduction, and leads to a deceleration and even a potential stagnation of slabs at ~300 km, just like the effects of metastable pyroxene, olivine, and plagioclase on
the slab dynamics (e.g., Hogrefe et al. 1994; Kawakatsu and Yoshioka 2011; Agrusta et al. 2014; Pakhomova et al. 2020).

The high $P-T$ Raman experimental results have potential implications for the effects of subduction-zone fluids on K-feldspar. Seismic studies have shown that a amounts of water could be transported along the subducted slabs deep into the mantle (Kawakatsu and Watada 2010). Although most of the water is released from the oceanic crust at depths of 150-200 km (Iwamori 2007), under cold subduction conditions, water could be stored in hydrous minerals, or enter deeper mantle as nominally anhydrous minerals containing hydroxyl group (OH) (Wang et al. 2020).

Our study indicates that K-feldspar with high Al coordination number is relatively more stable than that with low coordination number in the deep Earth enriched OH fluids (such as water). The phase relations of K-feldspar in the ultracold and hydrous subducting slab are shown in Figure 8 (b). At temperature above 350-400 °C subducting environments, K-feldspar with low coordination structure cannot resist fluid metamorphism and rapidly decomposes into the coesite-containing assemblage at depth above 135 km. An obvious dispersion of sample in ME/MEW/H$_2$O after the decomposition was observed in the experiment, so we infer low-temperature fluid metamorphism of K-feldspar may potentially affect continental slab breakoff and seismic activities. Besides, quartz is highly soluble in metamorphic fluids, so the assemblage containing coesite may be difficult to deeper subduction in metamorphic environments, which inhibits its further phase transition to form K-holl-I. Thus, the well-known phase transitions of K-feldspar $\rightarrow$ Ky + Wd + Coe/St $\rightarrow$ K-holl-I maybe
only occur within dry and cold slabs. However, in the subduction zones where metastable phases can be preserved, K-feldspar firstly transforms into metastable phase which has higher structural stability to withstand fluid metamorphism and is stable at least at close to mantle transition zone, where are enriched in OH. So metastable K-feldspar could survive to deeper than previously expected, and more likely further subducts and transforms into K-holl-I. The phase transitions of K-feldspar $\rightarrow$ metastable phase $\rightarrow$ K-holl-I could occur in both dry and hydrous slabs. K-holl-I is considered to be the most abundant phase in a continental crust composition in the upper and lower mantle. Studies about the existence of K-holl-I was mostly carried out in a high-pressure multi-anvil apparatus, in which samples were firstly compressed up to a target pressure and then heated up (e.g., Wu et al. 2009; Ishii et al. 2012). So the metastable phase transition process may has been ignored. The phase behavior of metastable K-feldspar in ultracold subduction could help us to explore the possible formation paths and conditions of K-holl-I, existing depth of K-feldspar, and have further understanding of continental subduction.

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Figure 1. Schematic diagram of the sample assembly for synthesis (a), sample characterization of
K-feldspar by Raman spectrum (b) and X-ray diffraction (XRD) (c) under ambient conditions.
The black and red solid lines represent the measured spectra and the standard spectra, respectively.
Figure 2. Representative Raman spectra of K-feldspar at various pressures and ambient temperature, displayed in the frequency range of 100-800 cm$^{-1}$ (a), the pressure dependence of the Raman shift (b), and the full width at half maximum (FWHM) for the $Ic$ mode as a function of the pressure (c).
Figure 3. Representative Raman spectra of K-feldspar at various temperatures and ambient pressure, displayed in the frequency range of 100-1200 cm$^{-1}$ (a), and the temperature dependence of Raman bands of K-feldspar at ambient pressure (b).
Figure 4. Representative Raman spectra of K-feldspar under different high $P$-$T$ conditions within various PTMs (the PTMs are given in brackets), displayed in the frequency range of 100-800 cm$^{-1}$. The black, green, and blue solid lines represent K-feldspar, the assemblage containing coesite, and metastable K-feldspar, respectively. K-feldspar could be stable and do not decompose within the $P$-$T$ range (0-11.4 GPa, 20-430 °C), as shown with the black and blue lines. The green and blue lines indicate K-feldspar with high Al coordination number is relatively more stable than that with low coordination number in the enriched OH fluids.
Figure 5. Raman spectra of samples recovered from high $P$-$T$ to ambient conditions in different PTMs (the PTMs are given in brackets), displayed in the frequency range of 100-1200 cm$^{-1}$. Peaks with black, red, blue, green, and purple asterisk are the characteristic Raman peaks of K-feldspar (K-fsp), coesite (Coe), Muscovite (Mus), KHCO$_3$, and stishovite (St), respectively. The black and green solid lines represent K-feldspar and the assemblage containing coesite, respectively.
Figure 6. Phase diagram of K-feldspar constrained by high $P$-$T$ experiments. Squares, circles, pentagon, hexagon, erected triangles, right triangles, left triangles, rhombus and stars indicate the $P$-$T$ conditions where K-feldspar (K-fsp), wadeite + kyanite + coesite (Wd + Ky + Coe), wadeite + kyanite + stishovite (Wd + Ky + St), liquid (Liq), leucite + liquid (Lc + Liq), liquid + kyanite + coesite (Liq + Ky + Coe), hollandite (K-holl-I) and hollandite II (K-holl-II) are stable, respectively. Meanwhile, adding different colors to distinguish them more clearly. The black solid lines represent the phase boundaries determined by high $P$-$T$ experiments or from previous phase diagram, and the dotted lines indicate the extrapolated phase boundaries by limited data (Lindsley 1966; Zhang et al. 1993; Urakawa et al. 1994; Yagi et al. 1994; Nishiyama et al. 2005; Akaogi et al. 2004; Ferroir et al. 2006; Yong et al. 2006; Zhang et al. 1993; Akogi et al. 2004; Pakhomova et al., 2020). Green and blue lines denote the geothermal gradients at 2°C/km and 5°C/km, respectively, in subduction zones (Zheng and Hermann 2014; Zheng 2019).
Figure 7. Raman spectra of samples quenched from different P-T conditions.

Figure 8. A schematic diagram of the ultracold dry (a) and hydrous (b) subducting slab and the phase relations of K-feldspar. The phase transition of K-feldspar $\rightarrow$ Ky + Wd + Coe/St $\rightarrow$ K-holl-I at relatively high-temperature regions (> 650 °C) is from previous studies (e.g., Zheng and Hermann...
2014; Zheng 2019), while the other phase transitions (K-feldspar→metastable phase→K-holl-I, K-feldspar→Coesite-containing assemblage) are from this study. The figure is not drawn to scale.

K-fsp: K-feldspar; Ky + Wd + Coe/St: kyanite + wadeite + coesite/stishovite; K-holl-I: K-hollandite-I.

Table 1. Constants determined in the expression: \( v_P = v_{i0} + (\partial v_i / \partial P) \times P \), \( v_T = v_{i0} + (\partial v_i / \partial T) \times T \), the isothermal (\( \gamma_i T \)) and isobaric (\( \gamma_i P \)) mode Grüneisen parameters, and the intrinsic anharmonic mode parameter (\( \beta_i \)) of K-feldspar.

<table>
<thead>
<tr>
<th>Modes</th>
<th>( v_{i0} ) (cm(^{-1}))</th>
<th>( \partial v_i / \partial P ) (cm(^{-1})/GPa)</th>
<th>( \gamma_i T )</th>
<th>( v_{i0} ) (cm(^{-1}))</th>
<th>( (\partial v_i / \partial T) \times 10^2 ) (cm(^{-1})/K)</th>
<th>( \gamma_i P )</th>
<th>( \beta_i \times 10^5 ) (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>III(_a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>124.28(13)</td>
<td>-0.82(3)</td>
<td>4.56(1)</td>
<td>-</td>
</tr>
<tr>
<td>III(_b)</td>
<td>157.99(13)</td>
<td>5.32(45)</td>
<td>1.96(2)</td>
<td>158.33(13)</td>
<td>-0.52(5)</td>
<td>2.28(2)</td>
<td>-0.46(2)</td>
</tr>
<tr>
<td>II(_a)</td>
<td>283.15(16)</td>
<td>1.41(28)</td>
<td>0.29(3)</td>
<td>284.27(16)</td>
<td>-0.17(1)</td>
<td>0.42(1)</td>
<td>-0.19(1)</td>
</tr>
<tr>
<td>I(_a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>455.42(10)</td>
<td>-0.73(6)</td>
<td>1.12(11)</td>
<td>-</td>
</tr>
<tr>
<td>I(_b)</td>
<td>474.68(10)</td>
<td>2.13(7)</td>
<td>0.26(7)</td>
<td>476.42(9)</td>
<td>-0.28(2)</td>
<td>0.41(5)</td>
<td>-0.22(3)</td>
</tr>
<tr>
<td>I(_c)</td>
<td>513.48(2)</td>
<td>3.56(9)</td>
<td>0.40(6)</td>
<td>515.22(2)</td>
<td>-0.38(1)</td>
<td>0.51(3)</td>
<td>-0.16(1)</td>
</tr>
</tbody>
</table>

Notes: The frequency at room pressure (\( v_{i0} \)), pressure coefficients (\( \partial v_i / \partial P \)), and temperature coefficients (\( \partial v_i / \partial T \)) obtained in this study were used to calculate the mode Grüneisen parameters (\( \gamma_i T \), \( \gamma_i P \)) and intrinsic anharmonic mode parameter (\( \beta_i \)), using the isothermal bulk modulus (\( K_T \)) with values of 58.3(2.0) GPa (Allan and Angel 1997), and the volume thermal expansion coefficient (\( \alpha \)) with values of 1.44(8)×10\(^{-5}\) K\(^{-1}\) (Henderson 1979).
Supplementary Information

for the manuscript "A revisit to phase transition behavior of K-feldspar at high-pressure and high-temperature: Implications on metastable K-feldspar in cold subduction" by Chengcheng He et al.

Figure S1. Schematic cross-section of cell assembly for quenching experiments.
Figure S2. Representative Raman spectra of K-feldspar measured with increasing pressure in nitrogen (a) and H$_2$O (b). The decompression spectra as shown in (a) is nearly same with the spectrum at ambient condition, which reveals the phase transition of K-feldspar into metastable
phase under high was reversible. The spectra only displayed in the frequency range of 200-1200 cm\(^{-1}\) because of the intense Raman bands at 100 and 200 cm\(^{-1}\) of the pressure medium nitrogen. Another decompression spectra as shown in (b) is also similar with the spectrum at ambient condition, which indicates the reversibility of the not fully amorphization.

**Figure S3.** Pressure dependence of the Raman bands of K-feldspar at ambient temperature.
(c) K-feldspar at high P-T conditions in ME (11.4-13.9 GPa, 20-400 °C)

Recovered sample at ambient condition

K-feldspar

Metastable K-feldspar

(f) K-feldspar at high P-T conditions in MEW (4.5-5.4 GPa, 20-400 °C)

Assemblage containing ecserite

Recovered sample at ambient condition

K-feldspar
**Figure S4.** Raman spectra of the K-feldspar up to ~14.7 GPa, 430 °C within various PTMs. Raman spectra of K-feldspar at high $P$-$T$ in 4:1 ME mixture, 16:3:1 MEW mixture, helium, no PTM, and H$_2$O, respectively (a)-(e), (f), (g), (h), (i)-(j). N(1-7) are the new bands that may correspond to the assemblage containing coesite revealed in Raman spectra of the recovered
Figure S5. Raman spectra of K-feldspar during compressing (a), cooling (b), and decompressing (c) process.
**Figure S6.** Determination of Raman spectra of recovered sample from 430 °C, 6.7 GPa (compressed in ME) (a), 430 °C, 5.9 GPa (compressed in MEW) (b) and 400 °C, 5.9 GPa (compressed in H2O) (c) by comparing with standard Raman spectrum of possible substances. The standard Raman spectra of KHCO₃ was obtained by measuring its high purity powder (99.99%, Alfa Aesar), and the others were download from RRUFF database (https://rruff.info). The recovered sample from 430 °C, 6.7 GPa (ME) contain coesite, stishovite, and KHCO₃. The recovered sample from 430 °C, 5.9 GPa (MEW) contain coesite, muscovite, and KHCO₃. The recovered sample from 400 °C, 5.9 GPa (H₂O) contain coesite and muscovite. The possible substances corresponding to the sharp peaks at 900-1100 cm⁻¹ has not been determined yet, as shown in Figures (b-c).
Figure S7. Raman spectra of K-feldspar holding at 430 °C in H₂O for 1h.