Experimental study on the kinetics of magnesiohornblende dehydration and its implications

Han Kenan¹,², Yi Li¹, Wang Duojun², Zhang Ruixin², Chen Peng²

1. United Laboratory of High-Pressure Physics and Earthquake Science, Institute of Earthquake Forecasting, CEA, Beijing 100036, China
2. High pressure center, College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

Magnesiohornblende dehydration was studied using both high-temperature thermogravimetric analysis and high-pressure differential thermal analysis (HP-DTA). The high-temperature thermogravimetric analysis results revealed that magnesiohornblende dehydration at high temperatures could be divided into three steps: 848–1058 K, 1058–1243 K, and 1243–1473 K, and each step followed an \( n \)-order reaction (\( F_n \)). The dehydration process is characterized by an oxidation-dehydrogenation mechanism, and the dehydration of the last step can be explained as the direct decomposition of the hydroxyl groups connected to the magnesium ions. The HP-DTA of magnesiohornblende dehydration under pressures of 0.5, 1.0, 2.0, and 3.0...
GPa revealed the occurrence of two endothermic peaks, indicating that the dehydration occurs in two steps at high temperature and pressure. Our experimental results reveal that during subduction, the fluid released during the dehydration of magnesiohornblende may trigger earthquakes and cause high electrical conductivity anomalies in the subduction zones.

**Keywords:** magnesiohornblende; dehydration; thermogravimetric analysis; high-pressure differential thermal analysis (HP-DTA); subduction zones
INTRODUCTION

As one of the most complex and active zones in the Earth’s interior, subducted slabs carry water into the deep parts of the Earth where it can form different types of hydrous minerals at different depths (Tatsumi and Kogiso, 2003). The dehydration of hydrous minerals influences many geological processes and the geodynamics of the Earth, such as partial melting and earthquakes (Marschall and Foster, 2018). The dehydration of hydrous minerals in subduction zones is of great significance to understanding the physical and chemical properties of minerals and rocks, such as high electrical conductivity anomalies and seismic wave velocity anomalies (Dai et al., 2020; Hu et al., 2018; Ji et al., 2013; Ji et al., 2015; Jung et al., 2014; Kim and Jung, 2019; Wang et al., 2012).

Amphibole is an important double chain silicate mineral \((AB_2C_5T_5O_{22}W_2)\) in the oceanic crust, subducting slab, and metamorphic and igneous rocks (Hawthorne and Oberti, 2007). The mineralogical model of the continental crust indicates that the amphibole content of rocks can reach 35–40% (by volume) within 15–30 km of the surface (Christensen and Mooney, 1995). As one of the important reservoirs of fluids and volatiles, the amphibole content of amphibole-eclogite facies and amphibolite facies can reach 50–60% in subduction zones (Poli and Schmidt, 1995). Amphibole undergoes a series of metamorphic dehydration reactions during subduction, which affects the oxidation of the iron in the amphibole and the release of fluids into the lower
crust and mantle.

The thermal decomposition of amphibole group minerals has been previously studied and some progress (Kusiorowski et al., 2015; Kusiorowski et al., 2012; Li et al., 2022) has been made. As one of the common minerals with the a complex structure, Fe-dominant amphibole has mainly been used for technological applications such as insulation from heat and fire (Addison et al., 1962a; Addison et al., 1962b; Addison and Sharp, 1962; Addison and White, 1968; Ernst and Wai, 1970; Hodgson et al., 1965). Accordingly, the oxidation-dehydrogenation mechanism of crocidolite at high temperatures, structural changes, and the influences of the Fe\(^{2+}\) and Mg\(^{2+}\) contents have been widely studied (Phillips et al., 1988; Phillips et al., 1991; Ungaretti, 1980). Recent studies on the stability of amphibole have focused on riebeckite in sodic amphibole, which is a typical high-pressure mineral (Della Ventura et al., 2018; Oberti et al., 2016; Oberti et al., 2018; Ventura et al., 2017). The oxidation-dehydrogenation reaction of iron-bearing amphibole can occur as follows:

\[
2\text{Fe}^{2+} + 2\text{W(OH)}^- \rightarrow 2\text{Fe}^{3+} + 2\text{WO}_2^- + \sigma\text{H}_2
\]

where W is the W(hydroxyl)-site anions in the formulae AB\(_2\)C\(_3\)T\(_8\)O\(_{22}\)W\(_2\), \(\sigma\text{H}_2\) means the external H\(_2\). This reaction reveals the oxidation of ferrous iron is coupled with a loss of protons from the W(hydroxyl)-site simultaneously to balance the charge in the local region and produce external H\(_2\). In the oxidation-dehydrogenation of iron-bearing amphibole, dehydrogenation often occurs within a few hours (Hu et al., 2018; Manthilake et al., 2021; Ungaretti, 1980). Fourier transform infrared (FTIR)
spectroscopy and Raman spectroscopy studies have suggested that the oxidation dehydrogenation reaction is reversible within a definite but broad range of temperatures for iron-bearing amphibole (Della Ventura et al., 2018; Mihailova et al., 2021). Compared with Fe-bearing amphibole, the dehydration temperature of Mg-rich amphibole is thought to be 200–600 K higher, but the dehydration temperature of magnesiohornblende under high-temperature and high-pressure conditions is not well defined. In addition, the dehydration kinetics of Mg-rich amphibole at high temperatures has not been fully studied. Moreover, as the ferrous content increases, the $C2/m \rightarrow P2_1/m$ phase transition may occur during the heating of Mg-dominated amphibole (Welch et al., 2007), and the critical temperature decreases from ~600 K to 200 K (Ballaran et al., 2004; Marschall and Foster, 2018; Welch et al., 2007).

In this study, thermogravimetric analysis and high-pressure differential thermal analysis (HP-DTA) were used to study the kinetics of magnesiohornblende dehydration, and the dehydration temperature and kinetics of magnesiohornblende were confirmed.

**EXPERIMENTAL METHODS**

**Sample Material**

The material used in the experiments was magnesiohornblende crystals collected from Liaoning Province, China. The chemical compositions of the magnesiohornblende crystals were analyzed using an electron probe microanalyzer (Table 1). The magnesiohornblende crystals were washed and ultrasonicated for 30 min and then ground into powder using an agate mortar. Various grains with different sizes were
separated from the powdered materials according to Stokes’s law (Ferguson and Church, 2004). Particles with diameters ranging from 5 to 10 μm were selected for use in the experiments and were stored above 393 K in a vacuum oven for one week to fully remove the absorbed molecular H₂O.

Thermal Analysis and Determination of Kinetic Parameters

Thermogravimetric (TG) analysis was performed to determine the reaction mechanisms and kinetic parameters using the STA449 F5 device at the University of Chinese Academy of Sciences. Magnesiohornblende dehydration was measured using non-isothermal and constant heating rates (10, 20, and 40 K/min). The samples were placed in corundum sample holders and heated at 303–1573 K in a constant air atmosphere (20 ml/min). The purge gas was nitrogen, with a flow rate of 60 ml/min. The sample weight of each non-isothermal experiment was 20 mg, and the error of the weight was less than 0.1 mg. The data were collected at an interval of 1 s.

In the thermal analysis of the kinetics, isothermal or non-isothermal conditions were adopted to study the kinetics of the dehydration of the materials (Liu et al., 2019; Wang et al., 2015). To describe the dehydration progress under non-isothermal conditions, the mass fraction of the released volatiles (α) is defined as:

\[ \alpha = \frac{m_0 - m_t}{m_0 - m_f} \]  

(1)

where \( m_t \) is the mass at time \( t \), and \( m_0 \) and \( m_f \) are the initial and final masses of the sample.
The general rate equation and integral form of the rate equation are as follows:

\[ Rate = \frac{d\alpha}{dt} = kf(\alpha), \]  

\[ G(\alpha) = kt, \]  

(2) \hspace{1cm} (3)

where \( t \) is time; \( k \) is the rate constant; and \( f(\alpha) \) and \( G(\alpha) \) are the mechanism function and integral form of the mechanism function, respectively. \( k \) depends on the temperature \( T \), and the relationship between \( k \) and \( T \) can be expressed using the Arrhenius equation:

\[ k = A \exp(-E/RT). \]  

(4)

Under non-isothermal conditions, the heating rate \( \beta = \frac{dT}{dt} \) can be substituted into Equation 2 to obtain the non-isothermal rate equation:

\[ \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT. \]  

(5)

After the integration of Equation 5, an integral form of the general rate equation under non-isothermal conditions can be obtained (Liu et al., 2019; Ozawa, 1965; Wang et al., 2015):

\[ G(\alpha) = \frac{A}{\beta} \int_0^\alpha \exp\left(-\frac{E}{RT}\right) dT, \]  

(6)

where \( E \) is the apparent activation energy, \( A \) is a pre-exponential factor and \( R \) is the gas constant. The Flynn-Wall-Ozawa (FWO) method (Flynn and Wall, 1967; Ozawa, 1965; Ozawa, 1986), a model-free method, was used to determine the kinetic parameters including apparent activation energy (\( E \)), and pre-exponential factor (\( A \)) of magnesiohornblende dehydration:
The apparent activation energy $E_a$ can then be determined by plotting $\ln\left(\frac{d\alpha}{dt}\right)$ versus $1/T$ for each activation energy. Apparent activation energy is based on many effects that produce a cumulative result, which is similar to the concept of activation energy but relates to the probability of not exceeding some measurable attribute (Calderon-Cardenas et al., 2020). Dehydration reaction involves several processes, therefore, the overall apparent activation energy of the reaction need to be determined by averaging the apparent activation energy derived from $\ln(\frac{d\alpha}{dt})$ versus $1/T$ at different $\alpha$.

Another kinetic calculation method for thermal analysis is the model method, in which different reaction mechanisms are selected to fit the TG data, and then, the best reaction mechanism is determined based on the obtained apparent activation energy $E_a$

\[
\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[Af(\alpha)\right] - \frac{E}{RT}.
\]

High-Pressure Differential Thermal Analysis

All of the high-pressure experiments conducted in this study were conducted using the cubic-anvil high-pressure apparatus installed at University of Chinese Academy of
Sciences. The pressure calibrations were performed using the melting temperatures of sodium at different pressures (Akella et al., 1969), and the uncertainty in the pressure was estimated to be less than 0.11 GPa (Shen et al., 2020). A schematic diagram of the experimental apparatus used for the HP-DTA is shown in Figure 1. A pyrophyllite cube with a side length of 32.5 mm and a central hole diameter of 14.2 mm was used as the pressure transfer medium. Two layers of stainless steel foil were selected as the furnace, and a layer of Al$_2$O$_3$ insulating tube was placed between the stainless steel foil and the soaking pipe for insulation purposes. The H-type soaking tube was constructed of nickel (Ni) to ensure heat stability at high temperatures. Alumina powder was used as a reference sample for the thermoelectric potential measurement of the magnesiohornblende. The alumina powder and the magnesiohornblende were loaded in the upper and bottom parts of the H-type tube. A welded K-type thermocouple (NiCr-NiSi) was symmetrically inserted into the center of the magnesiohornblende and alumina powder at an interval of 8 mm to measure the temperature, and the uncertainty of the temperature was less than ±5 K. Before the experiment, the pyrophyllite, pyrophyllite plugs, and Al$_2$O$_3$ insulating tube were heated at 1173 K for 10 h to ensure complete dehydration.

Two digital multimeters were used to record the thermoelectric potential difference between the magnesiohornblende and alumina powder at 0.5, 1.0, 2.0, and 3.0 GPa. The temperature of the alumina powder during the heating was also recorded using one of the digital multimeters. The two digital multimeters automatically recorded the...
temperature, and their accuracy reached $10^{-13}$ V and $10^{-5}$ K. In the four experiments, the materials were heated to 773 K at a uniform rate for 2 h and then heated to 1473 K at a rate of 20 K/min.

**RESULTS**

Figure 2 shows the TG and DTG (the first derivative of TG curve over time) curve of the magnesiohornblende in the air atmosphere. Magnesiohornblende dehydration occurred in the temperature range of 848–1473 K, while the TG curve shifts regularly with increasing heating rates due to thermal hysteresis (Masumoto et al., 2018). The average mass loss under the different heating rates was 2.16 wt.% (the water content of amphibole was approximately 2.20 wt.%).

Combining the mass loss of the TG curve and the mass loss rate of the DTG curve, our study suggests that the first stage of magnesiohornblende dehydration occurs at 848–1058 K, which accounts for 25% of total mass loss (Table 2), where the lowest position of the DTG curve is the temperature at which the dehydration rate is fastest. As the DTG curve flattens out, the first stage of the reaction ends. The same phenomenon can be observed for the second and third stages of magnesiohornblende dehydration at 1058–1243 K and 1243–1473 K, yielding a total mass loss of 25% and 60%, respectively (Table 2). It is noteworthy that the experimental temperature has already prompted the start of the third stage of the reaction before the end of the second stage.

The fitting results for the kinetic parameters (Table 2) of the different reaction
mechanisms indicate that our TG data for the three steps are best fit by an \( n \)-order reaction \((Fn)\) for magnesiohornblende, with a correlation coefficient of 99.953\%. \( f(\alpha) = (1 - \alpha)^n \) and \( G(\alpha) = (1 - (1 - \alpha)^{1-n})(1 - n) \) are the differential and integral forms of the \( n \)-order reaction, respectively.

Table 2 presents the fitting results of the model method. As is shown in Table 2, the activation energy \( E \) of step 1 is 416.6 kJ/mol, the pre-exponential factor \( A \) is \( 1.58 \times 10^{22} \) s\(^{-1}\), and the reaction order \( n \) is 4.23. The activation energy \( E \) of step 2(1) is 411.4 kJ/mol, the pre-exponential factor \( A \) is \( 2.82 \times 10^{15} \) s\(^{-1}\), and the reaction order \( n \) is 2.3. The activation energy \( E \) of step 2(2) is 720.9 kJ/mol, the pre-exponential factor \( A \) is \( 2.51 \times 10^{27} \) s\(^{-1}\), and the reaction order \( n \) is 1.95. Using these fitting parameters, we recalculated the reaction progress at different heating rates and compared the results with the experimental TG data (Fig. 3(a)). The experimental data are in good agreement with the calculated results, despite there being small differences at high temperatures. The differences may be caused by the nucleation rate of the products. Therefore, we concluded that the kinetics of magnesiohornblende dehydration in three steps are well modeled by \( n \)-order reaction \((Fn)\).

The activation energy of magnesiohornblende dehydration in air obtained using the model-free method is 437–812 kJ/mol (\( \alpha = 0.1–0.85 \)) (Table 3). The model-free method uses the first-order reaction \((F_1)\) to fit the entire process of magnesiohornblende dehydration, with a correlation coefficient of 99.945\%. \( f(\alpha) = 1 - \alpha \) and \( G(\alpha) = -\ln(1 - \alpha) \) are the differential and integral forms of the first-order reaction, respectively. We
compared the experimental and calculated curves for the magnesiohornblende dehydration (Fig. 3(b)). Except for the deviation from the fitting results at high temperatures (>1350 K), the overall fit is relatively good. A problem that arises is that in the Arrhenius equation (Eq. 4) the activation energy is a fixed value for a single reaction mechanism, but the activation energy of magnesiohornblende calculated using the Friedman method fluctuates greatly. Therefore, a first-order reaction cannot reasonably describe the thermal decomposition of magnesiohornblende. We conclude that the model method fits the experimental data better than the model-free method.

Figure 4 shows the high-pressure differential thermal curve for magnesiohornblende at 0.5, 1.0, 2.0, and 3.0 GPa. Within the experimental temperature and pressure ranges, the alumina powder did not undergo physical and/or chemical reactions and did not produce a thermal effect. Therefore, the two peaks of the curve represent the two steps of magnesiohornblende dehydration. At low temperatures (<1000 K), there was no obvious difference in the differential thermal voltage signals of the magnesiohornblende and alumina powder. When the temperature and pressure conditions for the experiments extended beyond the stability field of magnesiohornblende, there was a temperature difference $\Delta T$ ($\Delta T < 0$) between the magnesiohornblende and alumina, and endothermic valleys were visible in the differential thermal curves of the experiments. The peak temperatures of the endothermic valley at 0.5 GPa were 1090 K and 1235 K for magnesiohornblende and alumina, respectively. The peak temperatures of the endothermic valley at 1.0 GPa were
1132 K and 1278 K. The peak temperatures of the endothermic valley at 2.0 GPa were
1161 K and 1313 K, and the peak temperatures of the endothermic valley at 3.0 GPa
were 1097 K and 1193 K.

Figure 5 shows the products at 3.0 GPa after quenching at the first and second
stages of magnesiohornblende dehydration at 1137 K and 1233 K, respectively. It can
be seen that products after dehydration are magnesiohornblende whose composition is
different from that of the starting material. The decomposition of magnesiohornblende
is involved in the oxidation-dehydrogenation process.

DISCUSSION

The dehydration temperature depends on the composition of the amphibole
(Fumagalli et al., 2009; Mandler and Grove, 2016; Phillips et al., 1988; Pirard and
Hermann, 2015; Ungaretti, 1980). For example, the different types of cations in position
B in the crystal structure of iron-poor and iron-bearing amphibole produce different
dehydration processes. Previous experiments on heat-treated amphibole (Phillips et al.,
1991) have shown that the Fe²⁺ at the M(1) and M(3) sites is oxidized during the
oxidation-dehydrogenation process to produce Fe³⁺ and one electron. In addition, some
of the Fe²⁺ ions at the M(2) and M(4) sites exchange with the Mg²⁺ ions at the M(1) and
M(3) sites and are then oxidized similarly (Ishida, 1998). Accordingly, the H⁺ connected
by O(3) is removed to ensure the charge balance in the local region. The reaction
products are H₂ and O²⁻. Previous studies have shown that the electrical conductivity
increases gradually as the iron content of the amphibole increases (Hu et al., 2018;
Schmidbauer et al., 2000; Shen et al., 2020; Wang et al., 2012; Zhou et al., 2011), and
the electrical conductivity is controlled by the electron produced by the oxidation of
Fe$^{2+}$ to Fe$^{3+}$. The delocalization of the e$^-$ and H$^+$ and the subsequent jumping are the
main reasons for the electrical conductivity of amphibole (jump between W anions).
Mg-rich and Fe-poor crocidolite decompose in steps during the thermal decomposition
process, which is mainly reflected in the fact that the higher the Fe$^{2+}$/Mg$^{2+}$ ratio is, the
more Fe$^{2+}$ is oxidized during the oxidation-dehydrogenation process (Addison et al.,
1962a; Addison et al., 1962b; Addison and Sharp, 1962; Addison and White, 1968;
Ungaretti, 1980).

According to the result of the kinetics of magnesiohornblende dehydration, we can
describe the various stages of dehydration at different temperature ranges. As is shown
in Figure 2 and Table 2, magnesiohornblende dehydration can be divided into three
steps: 848–1058 K, 1058–1243 K, and 1243–1473 K (Table 2). The results of the
thermogravimetric measurements show that from 848 to 1058 K the activation energy
is approximately 416 kJ/mol, and the mass loss (approximately 25% of the total mass
loss) can be explained by the oxidation-dehydrogenation of the magnesiohornblende.
Approximately 20% of the total mass loss occurs in the temperature range of 1058–
1243 K and may be caused by the decomposition of the hydroxyl group connected to
the Fe$^{3+}$ ion, which is not decomposed in the temperature range of 848–1058 K. The
activation energy of 411.4 kJ/mol is approximately equal to the activation energy of the
first step (416.6 kJ/mol), so the dehydration in this step is likely to be driven by
oxidation-dehydrogenation at high temperatures, which is probably due to the barrier formed by the delocalized H in the migration process. The mass loss in the temperature range of 1243–1473 K accounts for approximately 50% of the total mass loss and corresponds to an activation energy of 720.9 kJ/mol, which is much larger than the activation energy of the oxidation-dehydrogenation process. Therefore, the mass loss in this step may be due to the direct decomposition of the -OH connected to the Mg\(^{2+}\) ion in the inner part of the crystal. In this step, the dehydration associated with the migration of the Mg ion requires a large activation energy. Compared with using decomposition products to observe the decomposition steps in research on crocidolite, in this study the form of the kinetic parameters was used to more intuitively explain the changes in the decomposition mechanism during the dehydration.

Compared with the results of the thermogravimetric analysis, the magnesiohornblende dehydration under high-temperature and high-pressure conditions can be divided into two steps (Fig. 4): low- and high-temperature dehydration. The low-temperature dehydration curve is close to that of tremolite. In contrast, the high-temperature dehydration curve is much higher than that of tremolite. According to the stability of magnesiohornblende under subduction zone conditions obtained from the dehydration peak temperature during the high-pressure differential thermal experiment (Fig. 4), we found that magnesiohornblende may still partially exist within the stability region of tremolite. When the research object is calcic amphibole, we can ignore the factors that may affect the stability of amphibole, such as the alkaline content (Mandler...
and Grove, 2016; Pirard and Hermann, 2015). The stability phase diagram of calcic amphibole under high-temperature and high-pressure conditions shows that the stability of calcic amphibole increases with increasing Mg/(Mg+Fe\textsuperscript{2+}) content (Fig. 6). Previous studies (Gilbert, 1969; Oba, 1978; Thomas, 1982; Welch and Pawley, 1991) have pointed out that the stability of tremolite is the highest, that of hastingsite is the lowest, and that of tschermakite is between those of tremolite and hastingsite. Compared with the decomposition of the hydroxyl groups connected to the Mg\textsuperscript{2+} ions at high temperatures, the decomposition of the hydroxyl groups connected to the Fe\textsuperscript{2+} ions occur at relatively low temperatures, so the stability of tremolite, which has the highest Mg/(Mg+Fe\textsuperscript{2+}) content, is the highest. Dehydration of calcic amphibole under high-temperature and high-pressure conditions and the participation of oxygen should be consistent with that of magnesiohornblende, and its dehydration process can be divided into two steps, which has also been suggested by Shen et al. (2020), who identified the two peaks corresponding to dehydration by FTIR.

**IMPLICATIONS**

Petrological studies have revealed that there is amphibole/chlorite saturated peridotite at the base of the mantle wedge, which is formed from the dehydration of the underlying slab, including the subducting oceanic crust and the serpentinized oceanic mantle (Ono, 1998; Peacock, 1996). These hydrous peridotite layers at the base of the mantle wedge under the northeastern part of the Japanese arc migrated along the subducting slab to form a hydrous layer. The fluid released by the dehydration of the
phlogopite (K-rich) and metasomatic amphibole in the hydrous layer caused the basaltic magmatism of the Nasu and Chokai zones in northeast Japan (Ito and Tatsumi, 1995; Ujike, 1988). But Fumagalli et al. (2009) studied the phase relations between phlogopite and amphibole in metasomatized peridotites and concluded that the decomposition of peridotite leads to more K in phlogopite entering amphibole and generating Ca-amphibole. Tremolite (calcic amphibole) is considered stable at higher temperatures than antigorite in the first ~180 km of depth (Mainprice and Ildefonse, 2009). So the results of this study suggest that the upward migration of the fluids generated by the dehydration of calcic amphibole (the Fe$^{2+}$ content is less than the H$^+$ content) led to the formation of two parallel volcanic zones, Nasu and Chokai in northeast Japan. Geophysical observations have revealed the presence of many high conductivity anomalies in subduction zones, which are related to the dehydration of hydrous minerals. Thus, these high electrical conductivity anomalies are formed by fluid accumulation.

The liquids released from hydrous minerals may cause partial melting, seismic events, low-velocity anomalies, and high electrical conductivity anomalies. It has been suggested by previous studies (Hilairet et al., 2007; Liu et al., 2019) that earthquakes will occur if the dehydration rates are higher than that of the viscous relaxation. Therefore, we calculated isothermal dehydration kinetic models for magnesiohornblende at different temperatures (Fig.7). It can be seen that the dehydration time decreases with increasing temperature, and the
dehydration can finish within 40 mins at 1350 K. This fast dehydration could supply sufficient fluid to form interconnected networks in subduction zones.

The dehydration rates \( (V_{1/2}) \) of magnesiohornblende can be obtained from the half-time of the reaction \( (t_{1/2}) \):

\[
V_{1/2} = \frac{C H_2O}{t_{1/2}} \times \frac{\rho}{\rho_{H_2O}},
\]

where \( C_{H2O} \) is the water content of the amphibole, \( \rho \) and \( \rho_{H2O} \) are the densities of water and amphibole, and \( t_{1/2} \) is the half-time of the reaction when \( \alpha \) is equal to 0.5. The half-time of the dehydrogenation and dehydroxylation can be obtained from the isothermal model shown in Figure 7. The fluid production rate \( V_{1/2} \) under dehydrogenation is \( 2.9 \times 10^{-4}, 1.7 \times 10^{-3}, 5.4 \times 10^{-3}, 1.6 \times 10^{-2}, \) and \( 7.6 \times 10^{-2} \) m\(^3\) fluid m\(^3\) rock s\(^{-1}\) at temperatures of 900, 930, 950, 970, and 1000 K, respectively. The fluid production rate \( V_{1/2} \) under dehydroxylation is \( 1.4 \times 10^{-4}, 4.3 \times 10^{-4}, 2.0 \times 10^{-3}, 9.0 \times 10^{-3}, \) and \( 2.3 \times 10^{-2} \) m\(^3\) fluid m\(^3\) rock s\(^{-1}\) at temperatures of 1250, 1270, 1300, 1330, and 1350 K, respectively. Compared with the viscous relaxation of antigorite (3.0 \( \times \) 10\(^{-7}\) to 3.0 \( \times \) 10\(^{-12}\) s\(^{-1}\) (Hilairet et al., 2007), the fast dehydration of magnesiohornblende could cause earthquakes in subduction zones.

Hu et al. (2018) measured the electrical conductivity of magnesiohornblende (0.5–2.0 GPa and 623–1173 K) and concluded that the enhanced electrical conductivity of magnesiohornblende after dehydrogenation could explain the high electrical conductivity anomalies (>10\(^{-2}\) S/m) observed in slab-mantle wedge interfaces (Fig. 8).
In this study, magnesiohornblende samples with similar compositions were used for the experimental research (Table 1). It was found that as the temperature and pressure continuously increased, after the oxidation-dehydrogenation of the magnesiohornblende, the hydroxyl groups connected to the Mg\(^{2+}\) ions in the structure were subsequently decomposed. According to the research results for tremolite conductivity (Shen et al., 2020), the dominant conductive mechanism in the reaction:

\[
\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2(\text{tremolite}) = 2\text{CaMgSi}_2\text{O}_6(\text{diopside}) + 3\text{MgSiO}_3(\text{enstatite}) + \text{SiO}_2(\text{quartz}) + \text{H}_2\text{O(gas)}
\]

dehydroxylation of tremolite may cause high electrical conductivity anomalies (maximum value of 1 S/m). Therefore, the high electrical conductivity anomalies caused by the magnesiohorblende dehydration in the slab-mantle wedge region may be dominated by oxidation-dehydrogenation and dehydroxylation. When Fe\(^{2+}\) and Mg\(^{2+}\) exist in calcic amphibole and the Fe\(^{2+}\) content is less than the H\(^+\) content, we believe that calcic amphibole will dehydrate in two steps (similar to magnesiohornblende), and the high electrical conductivity anomaly produced by this decomposition can be explained by two mechanisms. Therefore, the dehydration of amphibole could explain the high electrical conductivity anomalies at depths of ~180 km in subduction zones.

**Acknowledgments**

We thank Junjie Dong and an anonymous reviewer for their constructive reviews. This research was supported by the Natural Science Foundation of China (NSFC) Major
Research Plan on West-Pacific Earth System Multispheric Interactions (project number: 91958216), NSFC (project number: 41874104) and the Fundamental Research Funds for the Central Universities.

REFERENCES CITED


Kusiorowski, R., Zaremba, T., Gerle, A., Piotrowski, J., Simka, W., and Adamek, J.


Oba, T. (1978) Phase relationship of Ca₂Mg₃Al₂Si₆Al₂O₁₉(OH)₂-Ca₂Mg₃Fe³⁺₂Si₆Al₂O₁₉(OH)₂ join at high temperature and high pressure—the stability of tschermakite. Journal of Faculty of Science, Hokkaido University, 18, 339-350.


Ono, S. (1998) Stability limits of hydrous minerals in sediment and mid-ocean ridge


Figure captions

FIGURE 1
Schematic diagram of the experimental setup of the high-pressure differential thermal analysis.
The furnace was composed of two layers of stainless steel foil. The soaking tube was constructed of nickel to ensure stability at high temperatures. A digital multimeter was used to record the thermoelectric potential difference in the circuit and the temperature of the alumina powder.

FIGURE 2
TG and DTG curves for magnesiohornblende at different heating rates.
The black, red, and green lines represent the reaction progress for heating rates of 10, 20, and 40 K/min, respectively. The numbers are the heating rates.

FIGURE 3
Experimental and calculated curves obtained using (a) the model method and (b) the model-free method.
The solid line and dotted line represent the experimental data and calculated data, respectively. For the model-free method, the experimental data are fit by the first-order reaction ($F_1$), which shows a large difference between the experimental and calculated data. In contrast, for the model method, the experimental and calculated data agree well.

FIGURE 4
High-pressure differential thermal curves for magnesiohornblende at 0.5, 1.0, 2.0,
and 3.0 GPa.

Magnesiohornblende dehydration is an endothermic reaction, and two peaks in the curve at high temperatures and high pressures represent the two steps of the dehydration process.

FIGURE 5

Backscattered electron (BSE) image of the products within the first and second stages of magnesiohornblende dehydration under the 3.0 GPa.

(a) BSE image of the first stage (1137 K) of magnesiohornblende dehydration. (b) BSE image of the second stage (1233 K) of magnesiohornblende dehydration.

FIGURE 6

The stability of calcic amphibole under subduction zone conditions.

The red circles and blue squares represent the first and second peak values of the thermal decomposition in the high-pressure differential experiment, respectively. Hastingsite, \( \text{NaCa}_2\left(\text{Fe}^{2+}\text{Fe}^{3+}\right)\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2 \); Tschermakite, \( \text{Ca}_2\left(\text{Mg,AlFe}^{3+}\right)\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2 \); and Tremolite \( \text{Ca}_2\text{Mg}_3\text{Si}_8\text{O}_{22}(\text{OH})_2 \). The grey lines denote the geothermal gradients at 10, 20, and 30 °C/km in subduction zones.

FIGURE 7

Isothermal dehydration kinetic models for magnesiohornblende at different temperatures derived from the parameters of the non-isothermal experiments.

(a) decomposition rates at 848–1048 K based on the first dehydrogenation step and (b) 1243–1473 K based on the dehydroxylation step.
The electrical conductivities and dehydration reactions of amphibole with different Mg/(Mg+Fe$^{2+}$) contents under subduction zone conditions.

The electrical conductivities of Fe-dominant amphibole, Mg-Fe$^{2+}$-bearing magnesiohornblende, and Fe-free tremolite increase significantly during dehydrogenation and dehydroxylation (Hu et al., 2018; Shen et al., 2020). The blue and yellow areas are the electrical conductivity changes of amphibole with different Mg/(Mg+Fe$^{2+}$) contents on the subducted slab. Dehydrogenation and dehydroxylation occur during the magnesiohornblende dehydration, which may cause two electrical conductivity changes. The Fe-dominated amphibole undergoes dehydrogenation, and the Fe-free amphibole undergoes dehydroxylation. Dehydrogenation is the oxidation of Fe$^{2+}$ on the M(1) and M(3) octahedra to Fe$^{3+}$, the loss of H$^+$ ions bonded to the O(3) oxygen atom to balance the charge, and the reaction produces H$_2$. Dehydroxylation is the migration of protons to OH$^-$ of O3 site and combine to form water molecule. The upward migration of the fluids generated by the dehydration steps of calcic amphibole (the Fe$^{2+}$ content was less than the H$^+$ content) led to the formation of two parallel volcanic zones, Nasu and Chokai, in northeast Japan. Mg-Hb—magnesiohornblende, Amp—Amphibole, Tre—Tremolite.
Table 1

Chemical composition of magnesiohornblende determined using an electron probe microanalyzer. The chemical compositions of the magnesiohornblende and tremolite used in the electrical conductivity studies are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg-Hb [This study]</th>
<th>Mg-Hb (Hu et al., 2018)</th>
<th>Tremolite (Shen et al., 2020)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>1.56</td>
<td>0.38</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>16.33</td>
<td>14.29</td>
<td>25.65</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.65</td>
<td>3.66</td>
<td>0.09</td>
</tr>
<tr>
<td>SiO₂</td>
<td>49.77</td>
<td>50.56</td>
<td>58.28</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.42</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>CaO</td>
<td>11.45</td>
<td>20.43</td>
<td>12.99</td>
</tr>
<tr>
<td>FeO⁺</td>
<td>9.41</td>
<td>8.16</td>
<td>0.27</td>
</tr>
<tr>
<td>MnO</td>
<td>0.29</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.62</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>95.61</td>
<td>98.69</td>
<td>97.55</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>7.29</td>
<td>7.29</td>
<td>7.92</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3.57</td>
<td>3.07</td>
<td>5.20</td>
</tr>
</tbody>
</table>

\[ \frac{100 \text{Mg}}{\text{Mg} + \text{Fe}} \]

|        | 75.57   | 75.74   | 99.39   |

Note: Mg-Hb—magnesiohornblende. Twenty-three oxygen atoms were used to calculate the chemical formula of the crystal.
Table 2

Kinetic parameters calculated using the model method.

<table>
<thead>
<tr>
<th>Stage</th>
<th>T (K)</th>
<th>Mass loss (%)</th>
<th>E (kJ/mol)</th>
<th>A (1/s)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1058–848</td>
<td>25</td>
<td>416.60</td>
<td>1.58 × 10^{22}</td>
<td>4.23</td>
</tr>
<tr>
<td>2(1)</td>
<td>1058–1243</td>
<td>20</td>
<td>411.40</td>
<td>2.82 × 10^{15}</td>
<td>2.30</td>
</tr>
<tr>
<td>2(2)</td>
<td>1243–1473</td>
<td>55</td>
<td>720.90</td>
<td>2.51 × 10^{27}</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Note: E, A, and n are the apparent activation energy, pre-exponential factor, and the order of the reaction, respectively.
Table 3

$E$ and $A$ for different conversion rates calculated using the model-free method.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$E$ (kJ/mol)</th>
<th>$\Delta$</th>
<th>$A$ (1/s)</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>437.83</td>
<td>2.67</td>
<td>$7.40 \times 10^{21}$</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>663.75</td>
<td>48.79</td>
<td>$1.28 \times 10^{31}$</td>
<td>2.55</td>
</tr>
<tr>
<td>0.3</td>
<td>600.37</td>
<td>5.44</td>
<td>$7.19 \times 10^{22}$</td>
<td>0.24</td>
</tr>
<tr>
<td>0.4</td>
<td>539.85</td>
<td>1.54</td>
<td>$6.46 \times 10^{19}$</td>
<td>0.06</td>
</tr>
<tr>
<td>0.5</td>
<td>622.92</td>
<td>23.59</td>
<td>$1.17 \times 10^{23}$</td>
<td>0.97</td>
</tr>
<tr>
<td>0.6</td>
<td>669.95</td>
<td>27.62</td>
<td>$7.14 \times 10^{24}$</td>
<td>1.12</td>
</tr>
<tr>
<td>0.7</td>
<td>709.50</td>
<td>39.98</td>
<td>$2.2 \times 10^{26}$</td>
<td>1.60</td>
</tr>
<tr>
<td>0.8</td>
<td>767.12</td>
<td>66.22</td>
<td>$2.51 \times 10^{28}$</td>
<td>2.62</td>
</tr>
<tr>
<td>0.85</td>
<td>811.85</td>
<td>102.97</td>
<td>$1.01 \times 10^{30}$</td>
<td>4.05</td>
</tr>
<tr>
<td>Average</td>
<td>647.02</td>
<td>1.56</td>
<td>$1.56 \times 10^{10}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: $\alpha$ is the reacted fraction; $E$ is the apparent activation energy; $A$ is the pre-exponential factor; and $\Delta$ is an objective function, which was defined to describe the error between the experimental and fitting data.
Fig 2

Mass loss(%) vs. Temperature (K)

- TG
- DTG

10K/min
20K/min
40K/min
Fig 3

(a) Model method

- Experimental data
- Calculated data

(b) Model-free method

- 10K/min
- 20K/min
- 40K/min
Fig 5

(a) 1137 K

(b) 1233 K

10 μm
Fig 7

(a) and (b) show the temperature-time relationship with different temperatures indicated by the lines. The graphs demonstrate how the system evolves over time at various temperatures, with curves representing the progression towards equilibrium.

- **Fig 7a**: Temperature range from 900 K to 1000 K.
- **Fig 7b**: Temperature range from 1250 K to 1350 K.