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Stability of chlorite in the upper mantle

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ABSTRACT

Stability of chlorite in the presence of orthopyroxene under upper-mantle conditions has been thermodynamically examined in the model system $MgO-Al_2O_3-SiO_2-H_2O$ (MASH). All minerals were assumed to be pure in the MASH system. Calculation of the reaction curve took into account heat capacity (C_P), thermal expansion (αV), and isothermal compressibility (βV). If it is assumed that $\Delta\alpha V = \Delta\beta V = 0$, the stability of chlorite in the upper mantle is slightly pressure dependent; the upper stability curve for chlorite is located at 800 °C, 650 °C, and 500 °C, at 2.9 GPa, 4.2 GPa, and 5.0 GPa, respectively. On the other hand, the assumption that $\Delta\alpha V \neq 0$ and $\Delta\beta V \neq 0$ yields a more temperature-dependent curve for chlorite stability: 800 °C at 3.9 GPa and 700 °C at 5.5 GPa. The present calculation indicates that chlorite in down-dragged hydrous peridotite at the base of a mantle wedge decomposes at pressures of 3.0–3.5 GPa. Therefore, H_2O released from chlorite may play a partial role in producing magmas beneath a volcanic front that lies about 110 km above a subducted slab.

INTRODUCTION

Chlorite must crystallize during hydration processes in an ultramafic system and may be one of the main hydrous phases in both the lower crust and the upper mantle. Phase relations of chlorite have been examined in natural metamorphosed ultramafic rocks formed at low pressures or under lower-crustal conditions (e.g., Springer, 1974). However, very little is known about the stability of chlorite in the upper mantle, probably because chlorite is relatively uncommon in high-pressure hydrous ultramafic rocks that commonly contain amphibole and/or phlogopite. The stability of chlorite, which carries a large amount of water (ca. 13 wt%), should yield important information pertinent to the understanding of the distribution and circulation of water in the upper mantle.

In this paper, we examine the stability limit of chlorite in the upper mantle in terms of thermodynamic calculations and discuss the role of chlorite in magma genesis in subduction zones. Mineral abbreviations in the text and figures are after Kretz (1983).

Previous work

Staudigel and Schreyer (1977) conducted high-pressure experiments on the stability limit of 14-Å clinochlore, which is the thermally most stable mineral among Mg-rich chlorites, in the water-pressure range 1.0–3.5 GPa in the system $MgO-Al_2O_3-SiO_2-H_2O$ (MASH). Their results revealed that clinochlore disintegrates through strongly temperature-dependent reactions to forsterite, enstatite, spinel, and aqueous fluid at pressures below 2.0 GPa, that is, within the spinel peridotite field. In the garnet peridotite field, it breaks down to spinel, pyrope, forsterite, and aqueous fluid (Fig. 1). However, the reaction does not govern the stability limit of chlorite in a natural garnet peridotite, because chlorite is stable only under *P-T* conditions below those of the univariant curve of the reaction

$$\underset{\text{clinochlore}}{Mg_{10}Al_2Al_2Si_6O_{20}(OH)_{16}} + \underset{\text{enstatite}}{2Mg_2Si_2O_6} = \underset{\text{pyrope}}{2Mg_3Al_2Si_3O_{12}} + \underset{\text{forsterite}}{4Mg_2SiO_4} + \underset{\text{fluid}}{8H_2O}. \quad (1)$$

Delany and Helgeson (1978) calculated univariant curves for a number of dehydration reactions taking place

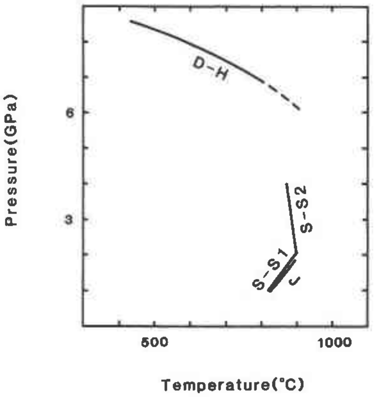

Fig. 1. Previous work bearing on chlorite stability at high pressures. S-S1: 14-Å clinochlore → enstatite + forsterite + spinel + H_2O (Staudigel and Schreyer, 1977). S-S2: 14-Å clinochlore → pyrope + forsterite + spinel + H_2O (Staudigel and Schreyer, 1977). D-H: 14-Å clinochlore → clinoenstatite + forsterite + spinel + H_2O (Delany and Helgeson, 1978). J: 14-Å clinochlore → enstatite + forsterite + spinel + H_2O (Jenkins, 1981).

in the subducted oceanic crust in the system K_2O-Na_2O-MgO-FeO-Al_2O_3-SiO_2-H_2O up to 10 GPa and presented the decomposition reaction of clinochlore. They argued that anhydrous assemblages after dehydration of 14-Å clinochlore at pressures up to 10 GPa are clinoenstatite, forsterite, spinel, and H_2O (Fig. 1). However, the assemblage enstatite + spinel can only be stable in the spinel peridotite stability field. It is stressed, therefore, that the dehydration curve of clinochlore after Delany and Helgeson (1978) is not applicable to the consideration of hydrous-phase relations in the upper mantle at pressures greater than 2 GPa.

Obata and Thompson (1981) made a first attempt to construct a petrogenetic grid for hydrous mafic and ultramafic rocks by combining the method of Schreinemakers with available experimental data in the model system CaO-MgO-Al_2O_3-SiO_2-H_2O (CMASH). For the chlorite-bearing reactions, Obata and Thompson chose the following from the grid:

$$\mathrm{Chl + Grt = Fo + Spl + Opx + H_2O} \tag{2}$$

$$\mathrm{Chl + Amp = Fo + Spl + Opx + H_2O} \tag{3}$$

$$\mathrm{Chl + An = Fo + Spl + Opx + H_2O} \tag{4}$$

$$\mathrm{Chl + Cpx = Fo + Spl + Opx + H_2O}. \tag{5}$$

Garnet, amphibole, anorthite, and clinopyroxene on the left-hand sides of the reactions and orthopyroxene on the right-hand sides of the reactions are CaO-bearing phases. However, the maximum stability of chlorite under spinel peridotite conditions, expressed by

$$\underset{\text{clinochlore}}{\mathrm{Mg_{10}Al_2Al_2Si_6O_{20}(OH)_{16}}} = \underset{\text{spinel}}{\mathrm{2MgAl_2O_4}} + \underset{\text{forsterite}}{\mathrm{2Mg_2SiO_4}} + \underset{\text{enstatite}}{\mathrm{2Mg_2Si_2O_6}} + \underset{\text{fluid}}{\mathrm{8H_2O}}, \tag{6}$$

should be adopted in the grid instead of Reactions 2 to 5, because the effect of CaO solubility in orthopyroxene on Reaction 6 is negligible in this temperature range (ca. less than 900 °C).

Jenkins (1981) determined the location of Reaction 6 and discussed the stability of chlorite lherzolite. As Reaction 6 shows, Jenkins's (1981, 1983) chlorite lherzolite is stable only in the spinel peridotite field, not in the garnet peridotite field.

Thermodynamic considerations

The aluminous phase in an upper-mantle peridotite changes from plagioclase through spinel to garnet with increasing pressure. Determining the stability of chlorite must take the coexisting aluminous phase into account; Reactions 1 and 6 define the stability of chlorite in a garnet peridotite system and a spinel peridotite system, respectively.

The dehydration curve of Reaction 6, which was experimentally determined by Staudigel and Schreyer (1977) and Jenkins (1981), is directly applicable to consideration of the stability of 14-Å clinochlore in spinel peridotites, because the dehydration products of clinochlore include the spinel peridotite minerals forsterite + enstatite + spinel.

In order to clarify the stability of chlorite in a garnet peridotite system, we examine the equilibrium conditions for Reaction 1 in terms of the equilibrium constant and activities:

$$\begin{aligned}\Delta G^0 = \Delta_f H - T\Delta S &+ \int_{298}^{T} \Delta C_P \, dT \\ &- T\int_{298}^{T} (\Delta C_P/T)\, dT \\ &+ P[\Delta V + \Delta(\alpha V)(T - 298) - \Delta(\beta V)P/2] \\ &+ 8RT \ln f_{H_2O} + RT \ln K\end{aligned}$$

$$K = \frac{(a^{grt}_{Mg_3Al_2Si_3O_{12}})^2 (a^{ol}_{Mg_2SiO_4})^4}{(a^{chl}_{Mg_{10}Al_2Al_2Si_6O_{20}(OH)_{16}})(a^{opx}_{Mg_2Si_2O_6})^2}\,.$$

Symbols are listed in Table 1; a_i^j is the activity of component i in phase j. As the behavior of H_2O differs markedly from that predicted from the perfect gas laws, the fugacity of H_2O (f_{H_2O}) tabulated by Burnham et al. (1969) up to 1.0-GPa pressures and Delany and Helgeson (1978) up to 10-GPa pressures are used for the present calculations. The thermodynamic data of minerals after Holland and Powell (1985) are also used (Table 2).

For the purpose of solving the equilibrium conditions for Reaction 1, the following simplified treatment may be sufficient. All phases treated here are assumed to be pure, although orthopyroxene can contain tschermakitic components. Thus, the equilibrium constant K can be unity.

Figures 2A and 2B show the calculated stability limit of chlorite in the presence of orthopyroxene in the MASH system. The results in Figure 2A are based on the assumption of $\Delta\alpha V = \Delta\beta V = 0$, and those in Figure 2B on $\Delta\alpha V \neq 0$ and $\Delta\beta V \neq 0$.

Because of the metastable extension of spinel peridotite assemblages into the garnet peridotite field, the univariant line of chlorite decomposition calculated by Delany and Helgeson (1978) is located at the highest P-T region (Fig. 1). Both the experiments by Staudigel and Schreyer (1977) and by Jenkins (1981) obtained similar dehydration curves of chlorite in the spinel peridotite field (Fig. 1). Since the Al_2O_3 content of chlorite is too high to decompose into garnet lherzolite minerals, the maximum stability of chlorite with more temperature-dependent reactions (S-S2 in Fig. 1) is wider than that of chlorite in peridotite in Figures 2A and 2B. It is suggested that chlorite in peridotite assemblages decomposes through a reaction with a positive dP/dT slope within the spinel peridotite field (Fig. 1) and through a reaction with a negative dP/dT slope under conditions corresponding to the garnet peridotite field (Figs. 2A, 2B).

Although chlorite has been recognized in only a few ultramafic rocks, it does crystallize under some upper-

Table 1. Symbols used in an equilibrium calculation

$\Delta_f H$	enthalpy of formation from the elements at 1 bar and 298 K
S	entropy at 1 bar and 298 K
V	volume at 1 bar and 298 K
C_P	heat capacity: $C_P = a + bT + cT^{-2} + dT^{-1/2}$, with T in kelvins
α	coefficient of thermal expansion
β	coefficient of isothermal compressibility
ΔG^0	Gibbs energy change for a reaction among pure end-member phases at the temperature and pressure of interest
K	equilibrium constant for a balanced reaction

Note: Thermodynamic properties are in units of kilojoules, kelvins, and kilobars.

mantle conditions. In the Ochiai-Hokubo ultramafic complex, southwestern Japan, a chlorite corona around chromian spinel was commonly observed even if the peridotite was almost free from serpentinization (Arai, 1978). Medaris (1980, 1984) also described the assemblage chlorite + orthopyroxene in Norwegian peridotite. These lines of evidence indicate that chlorite is stable under higher P-T conditions than both serpentine and talc.

Implication for magma genesis

A knowledge of the stability of hydrous phases in peridotite systems is essential to an understanding of magma genesis in the upper mantle, because H_2O released from hydrous phases drastically lowers the solidus temperature of peridotite. In particular, the origin of subduction-zone magmas has been related to the decomposition of hydrous minerals in subducted oceanic lithosphere (e.g., Fyfe and McBirney, 1975). Therefore, attention must be paid to the contribution of chlorite to the production of magmas in subduction zones. Tatsumi (1986, 1989) emphasized that the downgoing slab is anhydrous beneath a volcanic arc and proposed a mechanism in which hydrous peridotites, formed at the base of the fore-arc mantle wedge by the addition of slab-derived H_2O, are dragged downward on the slab. The mechanism implies that the stability of hydrous phases in a peridotite system strongly controls the position of magma generation in the mantle wedge.

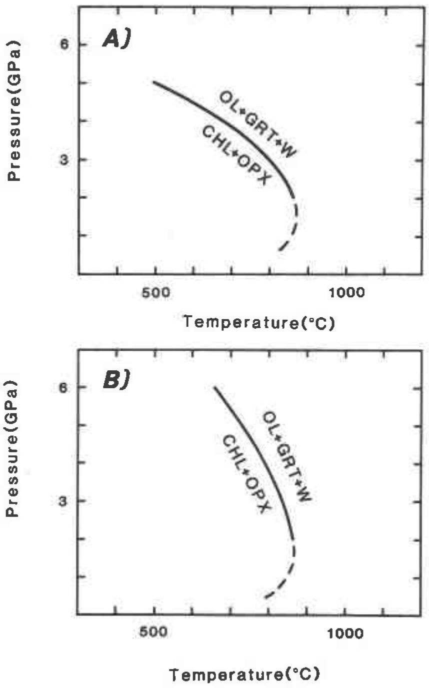

Fig. 2. Calculated stability limits of chlorite + orthopyroxene, based on the assumptions (**A**) $\Delta\alpha V = \Delta\beta V = 0$ and (**B**) $\Delta\alpha V \neq 0$ and $\Delta\beta V \neq 0$.

Figure 3 shows the calculated stability limits of chlorite in the MASH system together with decomposition curves of amphibole (AMP; Millhollen et al., 1974) and phlogopite (PHL; Sudo and Tatsumi, 1989) in a peridotite. Temperature distributions at the top (TMJ) and at 5 km below the top (TMJ5) of the subducted slab (Toksöz et al., 1971) are also shown in Figure 3. It should be noted that the decomposition of chlorite takes place under P-T conditions close to the maximum stability of amphibole in the down-dragged hydrous peridotite; both chlorite and amphibole break down at pressures of 3–3.5 GPa under the geothermal gradient shown on Figure 3. This pressure is equivalent to the depth of the base of the mantle wedge or the surface of the slab immediately beneath a volcanic front in most subduction zones [112 ± 19 (1σ) km; Tatsumi, 1986]. Therefore, it is suggested that generation of magmas beneath the volcanic front is governed by the dehydration of both chlorite and amphibole in the down-dragged hydrous peridotite. Chlorite decomposes through

Table 2. Thermodynamic properties used in this study

	Enstatite	Clinochlore	Forsterite	Pyrope	H_2O
H	−3090.08	−17742.12	−2173.02	−6284.49	−241.81
$S\ (\times 10^{-3})$	132.5	924.0	94.1	266.3	188.8
V	6.262	42.280	4.379	11.327	
a	0.3562	1.4494	0.2349	0.5450	0.0401
$b\ (\times 10^{-5})$	−0.299	23.074	0.107	2.068	0.866
c	−597	−40618	−543	−8331	488
d	−3.185	0.646	−1.906	−2.283	−0.251
$\alpha V\ (\times 10^{-5})$	18.0	136.0	16.0	28.0	
$\beta V\ (\times 10^{-3})$	4.6	76.0	3.2	7.6	

Note: Units are kilojoules, kelvins, and kilobars.

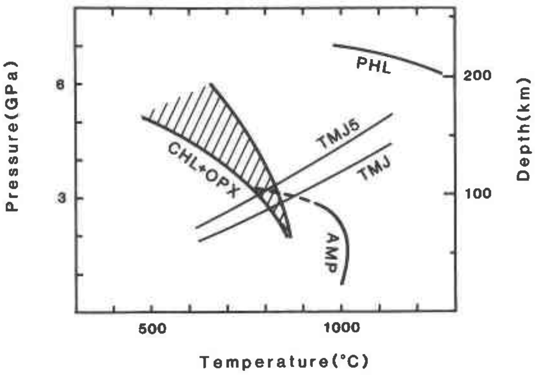

Fig. 3. Dehydration curves of phlogopite in a peridotite (PHL; Sudo and Tatsumi, 1989), amphibole in a peridotite (AMP; Millhollen et al., 1974), and chlorite + orthopyroxene in the MASH system (CHL + OPX). Temperature distributions at the top (TMJ) and at 5 km below the top (TMJ5) of the subducted slab (Toksöz et al., 1971) are also indicated.

a less pressure-dependent reaction than amphibole in a peridotite system (Fig. 3), which may yield the variety in depth of the subducted slab beneath the volcanic front. Phlogopite remains stable to deeper levels (Fig. 3), and its dehydration may be related to volcanism in volcanic arcs away from (behind) the volcanic front (Tatsumi, 1989; Sudo and Tatsumi, 1989).

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