Petrology of clintonite-bearing marbles in the Boulder aureole, Montana

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Abstract

The trioctahedral calcium brittle mica, clintonite, occurs locally in aluminous marbles near the intrusive contact of the Boulder batholith. Assemblages include clintonite-calcite-olivine-clinopyroxene-phlogopite and clintonite-calcite-olivine-spinel-phlogopite. Microprobe analyses of coexisting phases show clintonite to lie within the phase volume calcite-olivine-clinopyroxene-spinel, close to the MgSi-rich end of the synthesized solid solution. Phase relations are characterized by both continuous and discontinuous reactions. Discontinuous reactions between the observed phases result in a topology in \( \mu_{CO_2}-\mu_{H_2O} \) space which restricts the stability field of clintonite to relatively low \( \mu_{CO_2} \) and/or high \( \mu_{H_2O} \). The formation of clintonite was not related to metasomatism, but rather to reaction between calcite, olivine, clinopyroxene, spinel, and \( H_2O \) introduced from the intrusive body. In the Boulder aureole the formation of clintonite can be restricted to temperatures between 580° and 620°C with fluid compositions between \( X_{CO_2} \) of 0.05 and approximately 0.2.

Introduction

Trioctahedral calcium brittle micas, most appropriately referred to by the general name clintonite, form a solid-solution series which can be represented by the general formula

\[
Ca[(Mg,Fe^{2+})_{1+z}(Al,Fe^{3+})_{2-z}]Al_{4-z}Si_{10}(OH,F)_2
\]

Although such micas are rare, being found occasionally in thermally-metamorphosed impure carbonate rocks, they are interesting from a crystal-chemical point of view because of their high ratio of aluminum to silicon (>1) in the tetrahedral sites. Olesch (1975) has synthesized homogeneous clintonites over the compositional range \( z = 0.6 \) to 1.4. This range of solid solution encompasses and on the aluminum-rich side exceeds the observed variation in naturally-occurring brittle micas. Olesch and Seifert (1976) have determined the upper thermal stability limit of the solid-solution series, and have shown that such micas have a rather large \( P-T \) field of stability. In view of the large \( P-T \) stability field, they conclude that the critical parameters for clintonite formation are not fluid pressure or temperature but a rather special bulk-compositional requirements were met in the original sediment, and, except for changes in the chemical potentials of \( H_2O \) and \( CO_2 \), the formation of clintonite was not related to metasomatism, but rather to nearly isochemical reactions taking place in \( H_2O \)-rich fluids.

Clintonite parageneses

In the area west of Helena (Fig. 1), granodiorite of the Cretaceous Boulder batholith and Paleozoic sediments are in subvertical contact over a distance of about 20 km. The metamorphosed carbonate rocks are impure dolomitic limestones, typically silica-un-
Clintonite-bearing limestones have been found at four localities within 100 meters of the intrusive contact. Knopf (1953) reported an additional occurrence at the contact of the small satellite stock in the northern portion of Figure 1. The assemblages in these samples are either calcite-clintonite-olivine-clinopyroxene-phlogopite or calcite-clintonite-olivine-colorless spinel-phlogopite. As illustrated in Figure 3, clintonite typically occurs as randomly-oriented elongate blades 1 to 2 mm in length. When the brittle mica is abundant (ca. 20 modal percent) the rock takes on a microscopic jackstraw texture. The clintonite is characterized by a small optic angle ($2V_\alpha = 5^\circ$) and pleochroism ranging from colorless along $\alpha$ to very pale brown along $\beta$ and $\gamma$. Olivine and clinopyroxene occur as prismatic idiomorphic poikiloblasts composed of numerous subhedral grains with common extinction. The observed textural relationships indicate that clintonite formed by prograde metamorphism in equilibrium with its coexisting phases.

Based on the calculations of Jaeger (1957), the temperature at the immediate contact of the granodiorite is believed to have been between 600 and 700°C. Structural and stratigraphic relations summarized by Rice (1975) suggest that the total lithostatic pressure during metamorphism was approximately 1000 bars. The absence of either periclase or brucite...
Mineral chemistry

Electron microprobe analyses of coexisting phases in three samples containing the assemblage calcite-olivine-clinopyroxene-clintonite-phlogopite are given in Tables 1 and 2. Standards included a suite of natural and synthetic olivine, clinopyroxene, phlogopite, and anorthite, as well as a series of synthetic oxides. Data reduction was performed with a Bence-Albee-type correction procedure.

Olivine is typical of that in metamorphosed impure dolomites in being close to its ideal end-member composition (mole percent forsterite >95). In contrast, clinopyroxene contains significant amounts of aluminum and titanium. Below the analyses of clinopyroxene are listed calculated cations per six oxygens. All three analyses yield a cation sum which is slightly greater than 4.0, suggesting the presence of ferric iron. The data have therefore been recalculated into formula units normalized to 4.0 cations. In this procedure, additional oxygen is added to bring its sum to 6.0, and for each amount of oxygen added twice that amount of Fe$^{2+}$ is converted to Fe$^{3+}$ (Finger, 1972). The resulting formulae have ferrous to ferric ratios ranging from 4.0 to 1.0. Titanium is considered to be entirely Ti$^{4+}$. Combining Fe$^{2+}$ with Mg, and
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Fig. 4. Compositions of coexisting clinopyroxene and clintonite projected onto a portion of the plane SiO$_2$-Al$_2$O$_3$-MgO. Note that the composition of a given clintonite lies slightly to the left of a tie line connecting the compositions of coexisting clinopyroxene and spinel. The variation of clinopyroxene and brittle mica compositions implies attainment of chemical equilibrium and movement of the 3-phase triangle Fo-Cpx-Mi as a function of intensive variables, similar to that observed with 3-phase triangles on the familiar AFM projection (Thompson, 1957).

Origin of clintonite

Aside from the proximity of clintonite-bearing rocks to the intrusive contact, there is little evidence in either their mode of occurrence or composition to suggest that these rocks are of metasomatic origin. In particular, the presence of relatively low-variance assemblages is not indicative of mass transfer down externally-controlled chemical potential gradients. On the contrary, the occurrence of the isobaric

Fe$^{3+}$ with Al, calcium Tschermak's component (CaAlSiAlO$_4$) ranges from 5.3 to 7.1 mole percent, while the titanium component (CaTiAl$_2$O$_6$) ranges from 2.3 to 7.1 mole percent.

As with clinopyroxene, the mica analyses have been recast into formula units by normalization to a constant sum of cations. However, for these micas it makes very little difference if one normalizes to 8 cations or 22 oxygens. Phlogopite is similar in composition to that found in clintonite-free rocks throughout the contact aureole. There is no indication of calcium substitution in phlogopite, nor of potassium substitution in clintonite. The observed clintonite compositions (Si = 1.29 to 1.34 atoms) lie close to the MgSi-rich end of the solid-solution series synthesized by Olesch (1975) and are some of the most Al-poor natural clintonites. This feature indicates little or no diminution of the MgSi-rich end of the solid solution at temperatures down to about 600°C. The brittle micas appear to be strictly tri-octahedral in that there is no substitution toward the diocathedral calcium brittle mica margarite.
divariant assemblage calcite–olivine–clinopyroxene–spinel inward from isograd 4, and the observation of clintonite compositions plotting within this phase volume, are strong evidence that the clintonite formed by nearly isochemical reactions involving the observed phases and a CO$_2$–H$_2$O vapor.

The lack of adequate thermodynamic data for the clintonite solid-solution series precludes calculation of mineral equilibria in terms of $P$, $T$ and $X_{CO_2}$. It is possible, however, to gain a qualitative understanding of clintonite phase equilibria by an examination of the possible reactions between the phases observed in the Boulder aureole. The calculation of reactions between the observed phases is complicated by solid solution in clinopyroxene, tremolite, chlorite, and clintonite. Since all these phases exhibit solid solution of the type MgSi$_2$Al$_2$, the phase relations must be characterized by both continuous and discontinuous reactions (see J. B. Thompson, 1957; A. B. Thompson, 1976). Discontinuous reactions involve either the appearance or disappearance of a phase or phase assemblage, whereas continuous reactions involve only variation in the composition of the phases and will, in general, only be observed petrographically as a change in the relative proportions of phases with changing metamorphic grade. Depending on the formula chosen for the clintonite end-member, it is possible to derive two different sets of model reactions between the observed phases. To illustrate this point, consider the possible reactions between the phases calcite, forsterite, clinopyroxene, spinel, clintonite, and vapor. If the composition of the clintonite lies on the forsterite side of the clinopyroxene-spinel tie line (e.g., $M_i$, of Fig. 2) the formation of clintonite is described by the following general reaction:

$$\text{Fo + Cpx + Cc + Sp + H}_2\text{O} \rightleftharpoons M_i + \text{CO}_2 \quad (a)$$

On the other hand, if the composition of clintonite is chosen to lie to the right of the clinopyroxene-spinel tie line (e.g., $M_i$ of Fig. 2) the corresponding reaction forming clintonite is:

$$\text{Cpx + Cc + Sp + H}_2\text{O} \rightleftharpoons M_i + \text{Fo + CO}_2 \quad (b)$$

As shown in Figure 5, the chemographic relations and tie line flips resulting from these two discontinuous reactions are distinctly different. Although both reactions produce the 3-phase triangles (Fo–Cpx–$M_i$ and Fo–$M_i$–Sp) observed in the Boulder aureole, reaction (a) produces the 3-phase triangle clinopyroxene–clintonite–spinel (Fig. 5A). The presence of this 3-phase triangle is not consistent with the experimental data of Olesch and Seifert (1976), which show aluminum-rich clintonite ($z = 0.6$) coexisting with spinel and corundum (Fig. 5B) over a wide range of pressure and temperature. It thus seems likely that even though the analyzed clintonites lie to the left of the clinopyroxene–spinel tie line, the original formation of clintonite was in fact not due to a reaction of type (a) but rather a reaction of type (b).

In view of these considerations, an intermediate clintonite of composition CaMg$_2$Al$_3$Si$_2$O$_{10}$(OH) ($M_i$ of Fig. 2 with $z = 1.0$) was chosen as a model end-member. Stoichiometric coefficients for possible discontinuous reactions between this clintonite and the phases calcite, dolomite, forsterite, tremolite, diopside, clinochlore, spinel, CO$_2$, and H$_2$O have been calculated by the method of Finger and Burt (1972).

Although more than 70 reactions can be written between the above phases, a Schreinemakers multi-system analysis indicated that, for bulk compositions lying within the phase volume calcite–dolomite–diopside–spinel, only 18 are stable in the presence of a CO$_2$–H$_2$O fluid. Stoichiometric reaction coefficients for the stable equilibria are given in Table 3, and the $\mu_{CO_2}$-$\mu_{H_2O}$ topology is shown in Figure 6. Of two possible $\mu_{CO_2}$-$\mu_{H_2O}$ topologies, Figure 6 is considered to be stable because (1) natural assemblages in Al-free silicic dolomites require the stable existence of invariant point [Mi, Cte, Sp] (Trommsdorff,
Fig. 6. $\mu_{\text{CO}_2}$ vs. $\mu_{\text{H}_2\text{O}}$ diagram of end-member discontinuous reactions. Invariant point notation is that of phases absent. Shaded area shows the stability field for clintonite-bearing assemblages observed in the Boulder aureole. Chemographic diagrams are projections from CaCO$_3$, CO$_2$, and H$_2$O. X indicates observed 3-phase (+ calcite) assemblages.
1972; Skippen and Trommsdorff, 1975), and (2) the observation of the six-mineral assemblage corresponding to invariant point [Di,Mi] in the Boulder aureole (Rice, 1977) requires it also to be stable.

Figure 6 can be used to explain the formation of clintonite in the Boulder aureole. Examination shows that the observed parageneses are stable only in fluids characterized by a relatively low chemical potential of CO₂ and/or a high chemical potential of H₂O. The distribution of low-variance mineral parageneses in the outer and central portions of the aureole requires CO₂-rich fluids, and indicates buffering of the fluid composition by the local mineral assemblages. Field evidence suggests that isograd 3 is the result of reaction at invariant point [Di,Mi] to which the composition of the fluid was driven by the buffering process. At a slightly higher grade of metamorphism, clinopyroxene formed at the expense of calcic amphibole and calcite along isograd 4. Inward from isograd 4, the observed assemblages are restricted to lie below reaction 2 (Fig. 6). The innermost portion of the aureole is characterized by the isobaric divariant assemblages calcite-dolomite-forsterite-spinel and calcite-forsterite-clinopyroxene-spinel, which by themselves are not capable of buffering the fluid composition. The local occurrences of clintonite-bearing parageneses are related to the latter assemblage by the following reaction:

\[
2\text{Di} + \text{Cc} + 6\text{Sp} + 3\text{H}_2\text{O} = 3\text{Mi} + \text{Fo} + \text{CO}_2
\]

(14)

It is clear that bulk compositions capable of producing clintonite are present in these marbles, and that the only special conditions necessary for its formation are appropriate temperatures and the presence of a fluid characterized by a relatively low chemical potential of CO₂ or a high chemical potential of H₂O. These conditions were met locally near the intrusive contact, where initially CO₂-rich fluids were diluted by the addition of H₂O from the intrusive body. The nearly ubiquitous presence of phlogopite in apparent textural equilibrium in marbles both adjacent to and far removed from the intrusive contact does not support Bucher-Nurminen's (1976) suggestion that brittle micas form from reactions involving the breakdown of phlogopite under conditions of low \(K_2\text{O}\).

The formation of clintonite by the discontinuous reaction (14) would require the composition of the initially-formed clintonite to lie to the right of the clinopyroxene-spinel tie line. The fact that the analyzed clintonites lie in projection to the left of the tie line can be explained by subsequent movement of the 3-phase triangles Fo–Cpx–Mi and Fo–Mi–Sp toward more MgSi-rich compositions by continuous reactions between the phases Cc–Fo–Cpx–Mi and Cc–Fo–Mi–Sp, respectively. The observed compositional variation (Fig. 4) is consistent with such movement of the 3-phase triangles.

At the present time, it is not possible to accurately determine the location of the stable clintonite equilibria in terms of \(P\), \(T\), and \(X_{\text{CO}_2}\). Equilibrium (15) has been studied experimentally in mixed volatile (H₂O–CO₂) fluids by Hoschek (1976). Unfortunately Hoschek's experimental brackets, which cover a 30° temperature interval at 4000 bars pressure, are rather wide and do not place strict limits on the thermodynamic parameters which govern equilibrium (15). This fact, coupled with the lack of compositional
data for the solid-solution phases in the experiments, makes it impossible to extend the reaction to other pressures or to use it to calculate the equilibrium conditions for other clintonite reactions with any degree of confidence.

Realizing the large uncertainties involved with the clintonite equilibria, and also for that matter with chlorite equilibria (see Rice, 1977, or Bowman and Essene, 1977), an approximate isobaric $T$-$XCO_2$ diagram is presented in Figure 7. Although probably not correct in detail, this phase diagram describes the occurrence of clintonite in the Boulder aureole rather well. The $T$-$XCO_2$ location of equilibrium (15) and hence invariant point [Do,Tr] is consistent with, although not demanded by, the experimental brackets of Hoschek (1976), and with calcite–dolomite temperatures ($600^\circ\text{C} \pm 20^\circ\text{C}$) determined for samples in the innermost portion of the Boulder aureole. Figure 7 indicates that the field of stability for the observed assemblages is rather small. The stability field may be further limited by noting that, under the assumed $P$-$Z$ conditions, the absence of either periclase or brucite requires the fluid phase to have $XCO_2 > 0.05$ (Greenwood, 1975). The formation of clintonite in the Boulder aureole can thus be restricted to the temperature range of $580^\circ$ to $620^\circ$C with fluid compositions between $XCO_2$ of 0.05 and approximately 0.2.

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