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Notes

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COMMENT

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Zhu and Ogasawara (2002) interpret the textures and mineralogy of dolomitic marbles from the Kokchetav massif in terms of pressure-induced dissociation of dolomite (dol) to aragonite (ara) + magnesite (mag). On the basis of this assumption they postulate a minimum metamorphic pressure of 7.85 GPa, corresponding to subduction of at least 250 km depth.

I maintain that dolomite remained stable throughout the entire subduction-exhumation cycle in the dolomitic marble and that peak pressures reached at most 6 GPa. Dolomite is the main matrix mineral as well as the main mineral in inclusions in both garnet and zircon from the dolomitic marbles. Although magnesite is rarely found as inclusion (Shatsky et al., 1995), the assemblage ara + mag has never been observed so far. Zhu and Ogasawara (2002) do not report any magnesite. They suggest that magnesite survived as a metastable phase to conditions of about 2 GPa, 650 °C, where it partly reacted to $\text{MgO} + \text{C} + \text{O}_2$. The product MgO reacted then with majoritic garnet to form retrograde clinocllore. Apart from the resulting clinocllore, there is no other evidence supporting such an unnecessary complex process. Clinocllore is a very common mineral found as a result of retrogression of garnet and in this case can be attributed to the reaction: $\text{pyrope} + 2 \text{ dolomite} + 4 \text{ H}_2\text{O} = \text{clinocllore} + 2 \text{ calcite} + 2 \text{ CO}_2$. In fact, this reaction is in better agreement with the observed corrosion of garnet and dolomite and the equilibrium of newly formed calcite and clinocllore. The reported aragonite (Fig. 1E of Zhu and Ogasawara, 2002) is questionable. Calcite and aragonite have the same average atomic number (Z) and hence their backscatter emission should be similar, noting that garnet with a higher Z has a significantly lower backscatter emission than the supposed aragonite. Nevertheless, the reported carbonates with very low Mg and Fe contents probably originate from aragonite. The peak metamorphic assemblage is therefore garnet + clinopyroxene + dolomite \pm aragonite \pm diamond as previously suggested by Ogasawara et al. (2000). Peak metamorphic temperatures of ~ 950 °C in these dolomitic marbles are well constrained by garnet-clinopyroxene thermometry and are independently confirmed by the nitrogen aggregation state of diamond (eg., Hermann et al., 2001, and references therein). Figure 1 compiles relevant experimental phase relations. At 950 °C the assemblage dol + ara has a stability field confined to pressures below 5.5–6 GPa. Dol + ara react to Mg-calcite at 950–1000 °C, further confirming the peak temperature and minimum pressure of 4.5 GPa at 900 °C, within the stability field of diamond. The resulting field of peak metamorphism (A') is in strong contrast to the peak metamorphism (A) suggested by Zhu and Ogasawara (2002).

Zhu and Ogasawara (2002) use a complex reaction to explain the observed difference between peak and retrograde garnet compositions. This is again unnecessary because the retrograde garnet is buffered by coexisting calcite, dolomite, and chlorite according to the equilibria $\text{CaMg}^{-1}_{\text{garnet}} = \text{CaMg}^{-1}_{\text{carbonates}}$, and $\text{FeMg}^{-1}_{\text{garnet}} = \text{FeMg}^{-1}_{\text{chlorite}}$. The supposed majoritic character of garnet is not convincing because a Si content of 3.02 is within uncertainty of the analyses and the nor-

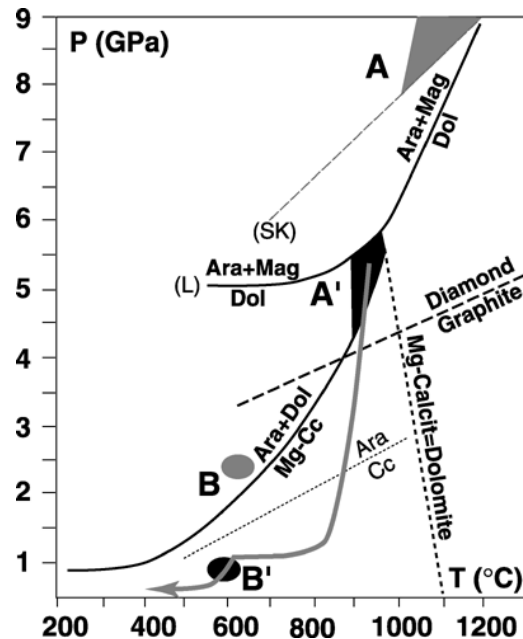


Figure 1. Experimental phase relations for dolomitic carbonates after Goldschmidt and Newton (1969), Irving and Wyllie (1975), Luth (2001), Buob et al. (2002), and personal unpublished data. Experimental study (L) of Luth (2001) on the reaction dolomite (dol) = aragonite (ara) + magnesite (mag), recently confirmed by Buob et al. (2002), has been preferred to study (SK) of Sato and Katsura (2001). Graphite-diamond transition is from Kennedy and Kennedy (1976). Shown retrograde evolution is taken from Hermann et al. (2001). Cc is calcite.

malization process is not distinguishable from a non-majoritic garnet. The difference in Si contents between peak and retrograde garnet might be real and is easily explained by the retrograde equilibrium $\text{MgSiAl}^{-2}_{\text{garnet}} = \text{MgSiAl}^{-2}_{\text{chlorite}}$. Hence, also on the basis of garnet composition, there is no need to have free MgO and consequently to propose metastable magnesite. The observed retrograde graphite can be explained by retrogression of diamond or by reduction of CO_2 from the metamorphic fluid. The retrogression likely occurred at pressure < 1.0 GPa and temperature ~ 600 °C (B'), in agreement with observed fluid influx in the country rocks of the dolomitic marble. The proposed stability field of retrogression (B) given by Zhu and Ogasawara (2002) is situated in the aragonite stability field and hence is inconsistent with their observation of stable calcite.

I conclude that the textures and mineral compositions presented by Zhu and Ogasawara (2002) do not support a minimum pressure of 7.85 GPa but a maximum pressure of 6 GPa. The described retrograde assemblage with calcite and clinocllore originates from decomposition of garnet and dolomite in the presence of fluids and does not require magnesite and MgO as precursors. Hence there is no evidence for dolomite dissociation in the Kokchetav dolomitic marbles.

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REPLY

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I appreciate the interest that Hermann has shown in our study of carbon recycled into deep Earth (Zhu and Ogasawara, 2002a). The work reported in that paper was accomplished in Ogasawara's laboratory at Waseda University; all samples were collected by Ogasawara, and the first author investigated these samples independently. The description and conclusion reached resulted from his own observation and ideas, hence the first author has the sole responsibility.

First of all, the rock I studied was dolomite marble, not dolomitic marble as Hermann commented. These two kinds of rocks are rather different (Ogasawara et al., 2000). For example, all clinopyroxene show exsolution texture in dolomite marble, whereas clinopyroxene in dolomitic marble is homogeneous.

Dolomite is the main matrix mineral as well as the main inclusion phase in garnet from dolomite marble. Based on this, Hermann's statement that dolomite remained stable during subduction is obviously wrong—aragonite + magnesite can easily form dolomite with pressure decrease or temperature increase (Luth, 2001). Only high-pressure phases trapped in garnet can be preserved in low-pressure environments due to overpressure of garnet just like coesite in garnet or in zircon. This is the reason that dolomite decomposition texture is preserved in garnet only. The suggestion by Hermann of a reaction between pyrope and dolomite to form clinocllore is not supported by petrographic observations. If that reaction had really happened, a reaction zone consisting of clinocllore + calcite on the boundary between garnet and matrix dolomite should be observed everywhere. This, however, is not the case in Kokchetav dolomite marble.

Aragonite characterized with remarkably high intensity on back-scattered electron (BSE) images was explained in the original paper

by its higher density. An additional factor could be the contents of some heavy trace elements. We believe the Si content of 3.02 for analyzed garnet with the range of 3.01–3.04 is not from the analytical uncertainty and normalization process. All garnet analyses constantly have $\text{Si} > 3.0$ in dolomite marble, whereas garnet in the reaction zone always contains $\text{Si} < 3.0$ (Fig. 2A in Zhu and Ogasawara, 2002a). The analytical method and conditions as well as the normalization process for these two kinds of garnet are exactly the same. Hermann might have been confused by the field B defined in our paper, which only represents the earliest stage of metamorphism in the graphite stability field. Further exhumation obviously led the slab into the calcite stability field. The minimum pressure-temperature conditions for the exhumation path were estimated to be 800 °C and 2.5 GPa (Ogasawara et al., 2000).

All published temperature estimates for rocks I studied were based on a pyroxene-garnet thermobarometer, which yielded >950 °C for clinopyroxene-garnet assemblage (up to 1200 °C; Okamoto et al., 2002). These values, however, could not represent the equilibrium temperatures for garnet and clinopyroxene, as clinopyroxene in dolomite marble developed exsolution textures. Another factor we must consider is that all pyroxene-garnet thermobarometers were designed based on experimental studies, which were carried out under pressures <4 GPa (mostly <3 GPa). Could we use such pyroxene-garnet thermobarometers to estimate temperatures of mineral pairs equilibrated at pressure >6 GPa? The answer is probably "no." Nevertheless, the occurrence of postcollisional lamproitic rocks in Kokchetav ultrahigh-pressure massif (Zhu et al., 2002) implies high-temperature environments in the upper mantle.

The experimental results of Luth (2001) produced a steep slope for the phase boundary of dolomite decomposition compared to the result of Sato and Katsura (2001). The difference in the reaction boundary reflects the different kinetics between decomposition and synthesis reactions (Shirasaka et al., 2002). Besides their large difference, however, these two experiments produced very similar results at high pressures. For example, dolomite decomposition occurred at 8 GPa (1100 °C) and 9 GPa (1200 °C) based on Luth (2001) and at 8.1 GPa (1000 °C) and 8.5 GPa (1100 °C) based on Sato and Katsura (2001). The high pressure estimate is consistent with phlogopite exsolution texture in super-silicic clinopyroxene found in dolomite marble (Zhu and Ogasawara, 2002b). Phlogopite exsolved from super-silicic clinopyroxene implies that the precursor of super-silicic clinopyroxene must be stable at pressures higher than 8 GPa.

Finally, I want to emphasize again that dolomite decomposition was defined by texture observations at first order in our paper. In order to explain the lack of magnesite and the formation of clinocllore and the compositional change of garnet in the reaction zone between dolomite inclusion and its host garnet, I logically hypothesized a complex reaction (the reaction 2) based on petrographic observations (Fig. 1 in Zhu and Ogasawara, 2002a). This hypothetical mechanism not only provides a reasonable explanation for phase relations observed in dolomite marble, but could also explain the scarcity of magnesite in Kokchetav ultrahigh-pressure rocks although magnesite occurs in many ultrahigh-pressure terrains (Zhang et al., 2002a, 2002b, and references therein).

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