Revision 1

Compositional zoning in dolomite from lawsonite-bearing eclogite (SW Tianshan, China):
Evidence for prograde metamorphism during subduction of oceanic crust

Ji-Lei Li,1,* Reiner Klemd,1 Jun Gao,2 and Melanie Meyer1

1GeoZentrum Nordbayern, Universität Erlangen–Nürnberg, Schloßgarten 5a, D-91054 Erlangen, Germany
2Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China

*Present address: GeoZentrum Nordbayern, Universität Erlangen–Nürnberg, Schloßgarten 5a, D-91054 Erlangen, Germany. E-mail: jilei.li@gzn.uni-erlangen.de
ABSTRACT

Dolomite with compositional zoning was discovered in carbonate-lawsonite-bearing eclogites in the Tianshan (ultra-)high-pressure/low-temperature metamorphic belt, northwestern China. The eclogite-facies dolomite occurs as matrix porphyroblast and as inclusion in garnet, both of which display the same chemical zoning pattern. The dolomite contains inclusions of calcite (probably after aragonite), magnesite, glaucophane, lawsonite (and its pseudomorphs), allanite, epidote, paragonite, phengite and omphacite. The chemical zoning in dolomite is well defined by a continuous core–to–rim Mg increase and Fe–Mn decrease. The concentrations of transition metal elements, REE and Y also decrease from core to rim of the dolomite. Thermodynamic modeling demonstrates that the Fe–Mg zoning of dolomite is largely temperature dependent and, thus, is interpreted as prograde growth zoning, which developed during subduction of carbonate-bearing oceanic crust. It is suggested that dolomite in equilibrium with garnet formed as a result of changing matrix compositions due to increasing temperatures. In addition, thermodynamic modeling demonstrates that during subduction at high-pressure conditions prograde-formed aragonite and dolomite were transformed to dolomite and magnesite. Furthermore, Fe-rich magnesite inclusions in matrix dolomite and in dolomite inclusions in garnet are shown to have formed during high-pressure conditions prior to peak metamorphic conditions and, therefore caution is warranted using Fe-bearing magnesite occurrences in eclogite-facies rocks as an unambiguous ultrahigh pressure indicator as previously suggested.

Keywords: prograde zoning, dolomite, magnesite, eclogite, high pressure, Tianshan
INTRODUCTION

Carbonates are common minerals in some blueschists and eclogites in (ultra-)high-pressure/low-temperature ((U)HP/LT) metamorphic terranes. Coesite inclusions in dolomite in eclogite-facies calc-silicate rocks and metabasalts from the Dabie ultrahigh-pressure (UHP) belt were interpreted as evidence for the subduction of continental crust (including sediments) to mantle depths (>100 km) and that coexisting dolomite and magnesite are stable mineral phases under UHP conditions (Schertl and Okay 1994; Zhang and Liou 1996). Coexisting magnesite, aragonite and calcite inclusions in dolomite have also been reported to occur in eclogites from several high-pressure (HP) and UHP metamorphic terranes and are regarded to be an UHP indicator (e.g., Wang and Liou 1993; Zhang and Liou 1994; Zhang et al. 2003). However, the coexistence of magnesite and dolomite as well as magnesite inclusions in dolomite in blueschists and eclogites were also interpreted to have formed under HP conditions (e.g., Klemd 2003; Smit et al. 2008; Li et al. 2012).

Compositional zoning is a distinctive feature that is commonly observed in petrographical and chemical studies of minerals, and it may provide important information on the minerals growth history and geological conditions during mineral formation. Compositional zoning, involving the variations in both trace and major elements, is most suitable for studying the dynamics of crystal growth (Tracy 1982). Different types of compositional zoning in dolomite, including concentric zoning, sector zoning and oscillatory zoning, were studied through imaging techniques such as cathodoluminescence (CL), back scattered electron imaging (BSE) and X-ray topographs in some sedimentary rocks (e.g., Farr 1989; Reeder and Prosky 1986; Reeder 1991; Wogelius et al. 1992; Shore and Fowler 1996). However, to our knowledge the compositional zoning of eclogite-facies dolomite has not been reported and
thermodynamically modeled yet. Nonetheless it was rarely observed in other metamorphic carbonates (cf., Jones and Ghent 1971; Reinecke et al. 2000).

In the present study, we present concentric Fe–Mg zoning of dolomite from HP lawsonite-carbonate-bearing eclogites in the southwest Tianshan (U)HP/LT metamorphic belt. The petrography and mineral chemistry of the dolomite and its inclusions were studied in detail by means of electron microprobe and laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS). Furthermore we conducted detailed textural and thermodynamic modeling studies of the dolomite and its inclusions in order to shed some light on the carbonate-phase formations and transitions in subducted oceanic crust.

GEOLOGICAL SETTING AND PETROGRAPHY

The Chinese Tianshan (U)HP/LT metamorphic belt extends for >200 km along the South Tianshan suture zone separating the Yili (-Central Tianshan) block to the north and the Tarim block to the south (see Fig. 1a in Li et al. 2012; Gao et al. 1998, 2011; Han et al. 2011). It mainly consists of blueschist-, eclogite- and greenschist-facies meta-sedimentary and some mafic metavolcanic rocks, the latter of which have N-MORB, E-MORB, OIB and arc basalt affinities (Gao et al. 1999; Gao and Klemd 2003; John et al. 2008). Peak metamorphism of some eclogites was estimated to have occurred under high-pressure conditions between 14 and 23 kbar at 480 and 580°C (e.g., Gao et al. 1999; Klemd et al. 2002; Wei et al. 2003; Li et al. 2012), while coesite relicts were identified in other eclogites or eclogite-facies rocks indicating that these rocks underwent UHP metamorphism (e.g., Lü et al. 2008, 2009; Lü and Zhang 2012). The intimate interlayering of HP and UHP rocks on a meter scale (Lü et al. 2009) was interpreted to be due to juxtaposition processes during subduction and exhumation in the subduction channel (Klemd et al. 2011). The timing of peak metamorphism was determined by multi-point Lu–Hf isochron ages from four blueschist- or eclogite-facies rocks
yielding consistent garnet-growth ages of ca. 315 Ma (Klemd et al. 2011). This age is in agreement, within error, with U–Pb SIMS ages of ca. 320 Ma on metamorphic zircon rims from eclogites (Su et al. 2010). White mica $^{40}$Ar/$^{39}$Ar and Rb–Sr ages of eclogite-facies metavolcanic rocks and omphacite-bearing blueschists cluster at ca. 311 Ma and were found to represent a major post-eclogite-facies episode of cooling or recrystallization (Klemd et al. 2005).

Marbles and carbonate-bearing HP metabasalts, metapelites are commonly observed in the Tianshan (U)HP/LT metamorphic belt. The occurrence of magnesite and calcite inclusions in dolomite in eclogites and metapelites was considered as evidence for UHP metamorphism (Zhang et al. 2002, 2003), but the petrological interpretation of carbonate/silicate mineral assemblages in (U)HP rocks is often highly controversial due to disequilibrium, crystallographical or textural considerations (e.g., Klemd et al. 1994; Klemd 2003; Smit et al. 2008; Hammouda et al. 2011). More recently, interlayered dolomite- and magnesite-bearing eclogite and blueschist in the Tianshan were interpreted to have coexisted at the same peak metamorphic HP conditions due to different bulk-rock compositions (Li et al. 2012).

This study focuses on the chemical zoning of dolomite from a previously described HP carbonate-lawsonite-bearing eclogite (sample L0910, Li et al. 2013). The peak metamorphic $P$–$T$ conditions of the eclogite are estimated at 580–590 ºC and 2.2–2.4 GPa. The eclogite consists of garnet (ca. 16 vol.%), omphacite (ca. 45%), carbonate (ca. 13%), white mica (ca. 13%), epidote (ca. 5%), glaucophane (ca. 3%), sulfide (ca. 2%), quartz (ca. 1%) and accessory minerals such as rutile, titanite, lawsonite and apatite. Porphyroblastic garnet contains barroisite/glaucophane, epidote, paragonite, quartz and albite in the core domain and omphacite, dolomite/magnesite and rutile in the mantle domain while the rim domain usually is inclusion-free. Occasionally, lawsonite and magnesite were found to be enclosed by dolomite inclusions in garnet porphyroblasts. Omphacite is often orientated parallel to the
weak foliation as defined by phengite. Furthermore, some glaucophane inclusions were
detected in the omphacite cores. Significantly, the eclogite contains ca. 13 vol.% carbonates,
mainly dolomite and minor magnesite and calcite (Table 1). The dolomite occurs as
idioblastic/subidioblastic coarse-grained porphyroblastic matrix mineral and as inclusion in
garnet (Fig. 1). The matrix dolomite (0.2–1 mm in diameter) contains inclusions of omphacite,
glaucophane, lawsonite, phengite, paragonite, epidote, allanite, chlorite, calcite, magnesite
and quartz (Fig. 1), while dolomite inclusions in garnet contain magnesite, paragonite and
lawsonite inclusions (Fig. 1a–b; cf., Li et al. 2013). Magnesite occurs as inclusion in matrix
dolomite and in dolomite inclusions in garnet (Fig. 1a–c). Calcite intergrown with chlorite,
phengite and paragonite occurs in the core of idioblastic matrix dolomite only (Fig. 1d).
Magnesite occasionally contains glaucophane inclusions (Fig. 1c). Epidote, which usually has
an allanite core, occurs as matrix mineral and as inclusion in dolomite prophyroblasts (Fig. 1d
and f). Lawsonite and its pseudomorphs (epidote-paragonite assemblages) were also
identified as inclusions in matrix dolomite (Fig. 1g).

ANALYTICAL METHODS

In situ major element compositions of carbonates and inclusion minerals were obtained
from polished thin sections by electron microprobe analysis (JEOL JXA 8200) at the
GeoZentrum Nordbayern (GZN) of the University Erlangen–Nürnberg, Erlangen, Germany.
Quantitative major element analyses were performed with an acceleration voltage of 15 kV, a
beam current of 15 nA, a beam diameter of 3 μm and 10–30s counting time, while qualitative
mapping of Ca, Fe, Mg and Mn in dolomite was conducted using an energy-dispersive X-ray
detector with an acceleration voltage of 15 kV, a beam current of 230 nA, a 3–5 μm pixel size
and dwell time of 100 ms. Natural minerals and synthetic oxides were used as standards, and
a program based on the ZAF procedure was used for data correction. Representative
microprobe analyses for the minerals in this study are presented in Table 1. In order to
determine the nature of the CaCO₃ polymorph occurring as inclusions in dolomite and garnet,
Laser-Raman spectroscopy was performed at Department of material in the same university.
The laser beam (wavelength of 533 nm) was focused on the CaCO₃ inclusions by means of
50× objectives of a polarizing microscope. The laser spot size was focused to 1 µm.

In situ trace element analyses of zoned dolomite and inclusions were performed by LA–
ICP–MS at the GZN using a single collector quadrupole Agilent 7500i ICP–MS equipped
with an UP193Fx Argon Fluoride New Wave Research Excimer laser ablation system. The
glass reference material NIST SRM 612 was used as standard for external calibration. LA–
ICP–MS measurements were conducted using a spot size of 25µm in diameter, a laser
frequency of 15 Hz and 0.63 GW/cm² and a fluence of 3.32 J/cm². The carrier gas consists of
a mixture of 0.65 l/min helium and 1.10 l/min argon. Acquisition time was 20 s for the
background and 25 s for the mineral analysis. The Ca-content of the carbonates determined
by EMP analysis was used as internal standard. Reproducibility and accuracy, which were
determined for NIST SRM 610, are usually <8% and <6%. The trace element concentrations
were calculated by GLITTER Version 3 (van Achterbergh et al. 2000). Representative trace
element analyses of the carbonate minerals are given in Table 2.

MINERAL CHEMISTRY

Garnet has a prograde compositional growth zoning with a continuous increase of the
pyrope component from 4.9 to 11.4 % and a decrease of the spessartine component from 4.2
to 1.6 % from the core towards the rim (Table 1). Omphacite inclusions in garnet and
dolomite and matrix omphacite have a similar jadeite component of between 32.8 mol.% and
46.5 mol.%. The Si–content of phengite is between 3.45–3.51 pfu and the Na-content of
paragonite at ca. 0.80 pfu (Table 1). The glaucophane and epidote-group minerals display
rather uniform compositions either as matrix or inclusion minerals (Table 1). For more
detailed microprobe data concerning the silicates in the eclogite see Li et al. (2013).

The dolomite studied here is a dolomite-ankerite solid solution (dolomite$_{s.s.}$) that contains
20–35 mol.% ankerite [CaFe(CO$_3$)$_2$] component due to the substitution of Fe$^{2+}$ for Mg (Table
1). This type of dolomite always contains small but variable amounts of Mn and less
commonly minor Sr, Pb, Ni and Zn (Table 2). LA–ICP–MS data show that the dolomite
contains high amounts of transition metal elements (e.g., Co: 18–60 ppm; Ni: 54–264 ppm
and Zn: 114–147 ppm), Sr (449–1633 ppm), Pb (2.17–27.8 ppm), P (23–28 ppm) and minor
Li, Ba, REE and Y (Table 2). The magnesite inclusions in the dolomite are magnesite-siderite
solid solutions (magnesite$_{s.s.}$) with a high siderite [FeCO$_3$] component (44–47 mol.%) and
about 1 mol.% CaCO$_3$ and even less MnCO$_3$ (Table 1). Magnesite hosts higher amounts of
transition metal elements (e.g., Co: 127–252 ppm; Ni: 181–533 ppm and Zn: 161–449 ppm)
but much lower Sr (0.110–5.17 ppm), Pb, HREE and Y concentrations than the dolomite
(Table 2). The HFSE concentrations in dolomite and magnesite are always below the
detection limit (Table 2). The CaCO$_3$ phase occurring as inclusions in dolomite is calcite
according to Raman spectrometry (Fig. 1d) and contains minor Mg, Fe and Mn contents
(Table 1). However, the stability of aragonite instead of calcite at HP/LT metamorphic
conditions is suggested by the thermodynamic modeling (see below) which is in agreement
with experimental studies (cf., Carlson 1980). Thus, the calcite inclusions are thought to have
formed at the expense of former aragonite at low-$P$ and high-$T$ during post peak metamorphic
conditions (e.g., Carlson 1980; Proyer et al. 2008).

COMPOSITIONAL ZONING OF DOLOMITE

Major elements
The zoning of dolomite is petrographically displayed by a change in color from core to rim in the BSE images (here displayed by changes of the gray intensity, Fig. 1d). The dolomite core contains inclusions of calcite (probably after aragonite), magnesite, paragonite, epidote, lawsonite, epidote and paragonite intergrowth (possibly after lawsonite) and occasionally omphacite. Omphacite, phengite and allanite inclusions occur in the darker rim domains (Fig. 1d and f). The Ca content of dolomite is rather homogeneous with a slight increase at the outer-rim (Figs. 2 and 3a). The Fe content continuously decreases from core (12.66 wt.%) to rim (7.51 wt.%) while the Mg content increases from 13.29 wt.% to 16.97 wt.% (Table 1). Thus $X_{Fe} = \frac{Fe}{(Fe+Mg)}$ decreases accordingly (Fig. 3a). The Mn content decreases from the dolomite core (0.53 wt.%) towards the inner-rim (0.18 wt.%) while it increases at the outermost rim (0.40 wt.%). In addition, a subtle oscillatory Mn zoning occurs in the inner-rim domain (Fig. 2). Magnesium and Fe show a good negative correlation in the $\text{Mg vs. Fe}$ plot (Fig. 3b). Interestingly, Mn shows a negative correlation with Mg and a positive correlation with Fe when neglecting the outer-rim Mn composition (Fig. 3c–d). The large scale mapping images document that the dolomite inclusions in garnet and matrix dolomite grains share the same compositional core–to–rim zoning pattern; however, the dolomite inclusions in garnet lack the (mantle-) rim domain in contrast to the matrix dolomite (Fig. 4).

**Trace elements**

The Sr and Pb concentrations decrease gradually from the dolomite core to the mantle and increase from the mantle to the inner-rim with an abrupt decrease at the outer-rim (Fig. 5a). Lithium, Ba and Sr display similar distribution patterns throughout the zoning profile (Fig. 5a). Manganese and Co exhibit a general decrease from core to rim and a slight oscillatory zoning at the inner-rim and an increase at the outermost rim (Fig. 5b). Zinc displays a flat
pattern. Vanadium, Cr and Ni concentrations decrease from core to mantle and then increase towards the rim with a significant drop at the outermost rim (Fig. 5b). In general, the dolomite core contains higher REE and Y concentrations than the mantle and rim (Fig. 5c and d). The chondrite-normalized REE diagram displays a MREE (especially Eu) enrichment relative to the LREE and HREE (Fig. 5d). The REE patterns presented here are in accordance with those of dolomite from other Tianshan eclogites (van der Straaten et al. 2008) but are quite different with the flat REE patterns in dolomite from Central Dabie coesite-bearing eclogites (Sassi et al. 2000). This discrepancy is believed to be due to different chemical bulk compositions of the protoliths (e.g. oceanic crust vs. continental crust) and/or the different rock mineralogy, which strongly controls the trace element distributions. The magnesite shows a relative HREE enrichment compared to the LREE and MREE (Fig. 5e).

THERMODYNAMIC MODELING

In order to obtain information on the carbonate-phase transitions as well as compositional variation of carbonates during HP/LT metamorphism, thermodynamic modeling of the carbonate-bearing eclogite L0910 was undertaken in the NMnCaKFMASCHO (Na2O–MnO–CaO–K2O–FeO–MgO–Al2O3–SiO2–CO2–H2O–Fe2O3) model system using the Perple_X software (Connolly 1990, 2005) and an internally consistent thermodynamic dataset (Holland and Powell 1998; and update) based on the effective bulk-rock composition (Table 3). Mineral solid-solution models are Gt(WPH) for garnet (White et al. 2007), Omph(GHP) for omphacite (Green et al. 2007), Amph(DPW) for amphibole (Dale et al. 2005), Mica(CHA) for phengite (Coggon and Holland 2002), Chl(HP) for chlorite (Holland and Powell 1998), Ep(HP) for epidote (Holland and Powell 1998), and F for H2O–CO2 fluid solution (Connolly and Trommsdorff 1991). In particular, the recently developed solid-solution model
$odCcMS(EF)$ for ternary Ca–Fe–Mg carbonates (Franzolin et al. 2011) was used to determine compositional variations in dolomite, the transition of carbonate minerals and the effect of Fe on carbonate stabilities during subduction conditions. For more details concerning the pseudosection calculations see Li et al. (2013).

A calculated phase equilibrium diagram is presented in Figure 6a. Omphacite, phengite and garnet are stable phases over the whole shown $P–T$ range, while lawsonite occurs in the low-$T$ range from which epidote-group minerals are absent. Amphibole is absent in the HT/HP stability fields. Dolomite is stable over a wide $P–T$ range, while magnesite occurs in the higher-pressure and aragonite in the LP/LT fields only (Fig. 6b). The modal amounts of dolomite, aragonite, magnesite, chlorite, amphibole, omphacite, lawsonite and garnet, along with the $X_{Fe}$ isopleths of magnesite$_{s.s.}$ and dolomite$_{s.s.}$ were contoured in the modeled pseudosection (Fig. 6). The modal amount of dolomite increases and that of aragonite decreases with increasing $P$ and $T$ in the aragonite-dolomite transition area (Fig. 6a). The modal amount of magnesite decreases and that of dolomite increases with increasing $T$ in the magnesite-bearing $P–T$ range of 550 to 600°C (Fig. 6a). The $X_{Fe}$ isopleths of magnesite$_{s.s.}$ are parallel to the $P$-axis and decrease in value from low to high temperatures in the amphibole-absence field (Fig. 6b). Similarly, the $X_{Fe}$ isopleths of dolomite$_{s.s.}$ are parallel to those of magnesite and also decrease from low to high temperatures in this field (Fig. 6b). The chemical changes as displayed by the $X_{Fe}$ contents of the dolomite$_{s.s.}$ are in agreement with the compositional variations observed in the zoned dolomite in the lawsonite-bearing eclogite (Figs. 2 and 3a). The $P–T$ paths of the studied eclogite and nearby eclogites (cf., Li et al. 2012, 2013) indicate that the low temperature/low pressure aragonite was progradely transformed to dolomite$_{s.s.}$ and then to dolomite$_{s.s.}$ and magnesite$_{s.s.}$ during increasing $P–T$ conditions (Fig. 6b, Table 3). The modal amount of omphacite (and of dolomite$_{s.s.}$ and magnesite$_{s.s.}$) increases at the expense of chlorite and amphibole with increasing $P–T$ conditions (Fig. 6b–d). Garnet
growth at the expense of lawsonite started at temperatures between 550 and 600°C (Fig. 6f and g).

DISCUSSION

Formation of dolomite and its prograde compositional zoning

Significant amounts of carbonates are introduced into mafic oceanic curst by hydrothermal alteration prior to subduction (e.g., Staudigel 2003). The crystallographically-bound CO$_2$ that preferentially occurs in carbonates in the slab rocks is carried down to great mantle depths without prominent decarbonation (Kerrick and Connolly 2001). Dolomitic carbonates are generally stable at pressures of up to 2–7 GPa in mafic eclogites (e.g., Yaxley and Green 1994; Molina and Poli 2000; Poli et al. 2009). High-pressure experimental data on the carbonate stability based on a basaltic composition in the presence of a H$_2$O–CO$_2$ mixed fluid demonstrate that calcite is stable at $P \leq 1.4$ GPa, dolomite at $P$ between 1.4 and 1.8 GPa, and dolomite and magnesite at $P \geq 1.8$ GPa (Molina and Poli 2000). These results are in accordance with the presented modeling which suggests the stability of aragonite at $T \leq 450$°C, $P \leq 1.7$ GPa, of dolomite at $1.7 \leq P \leq 2.1$ GPa and of dolomite and magnesite at even higher pressures (e.g., $P \geq 2.1$ GPa) (Fig. 6).

The occurrence of calcite (after aragonite)-chlorite inclusions in dolomite core domains in the studied sample (Fig. 1d) and calcite (after aragonite)-chlorite-dolomite inclusions in garnet cores (Fig. 1h) in adjacent eclogite (cf., Li et al. 2012) suggest the prograde formation of dolomite at LT–LP conditions ($400 \leq T \leq 480$°C, $1.5 \leq P \leq 2.1$ GPa) according to the continuous reaction:

\begin{equation}
\text{arag} + \text{chl} + \text{amp} \rightarrow \text{dol}_{x+1} + \text{omp} + \text{H}_2\text{O} \tag{1}
\end{equation}

this reaction corresponds to a decrease in the modal amounts of aragonite, chlorite and
amphibole and an increase of dolomite and omphacite in the pseudosection (see hatched area A; Fig. 6a and c–e). During increasing $P$–$T$ conditions dolomite partly reacts to magnesite (hatched area B) according to the reaction:

$$\text{dol}_{s.s.1} + \text{chl} + \text{amp} \rightarrow \text{mag}_{s.s.} + \text{omp} \pm \text{grt} + H_2O$$  \hspace{1cm} (2),

this reaction is displayed by increasing modal amounts of magnesite and omphacite (and garnet) which formed at the expense of chlorite and amphibole along the $P$–$T$ path (hatched area B in the pseudosection, Fig. 6a–e). This is supported by glaucophane inclusions in magnesite (Fig. 2c). The lawsonite and magnesite$_{s.s.}$ inclusions in matrix dolomite (Figs. 1c and g) and in dolomite inclusions in garnet (cf., Li et al. 2013) suggest that with increasing temperatures and pressures dolomite formed at the expense of magnesite (e.g., $550 \leq T \leq 600^\circ$C, $P \geq 2.1$ GPa) according to the continuous reaction:

$$\text{mag}_{s.s.} + \text{dol}_{s.s.1} + \text{law} + \text{omp} \rightarrow \text{dol}_{s.s.2} + \text{grt} + q + H_2O$$  \hspace{1cm} (3),

corresponding with gradually decreasing modal abundances of magnesite and lawsonite (Fig. 6a and f) and increasing modal amounts of dolomite and garnet (Fig. 6a and g) in the pseudosection (hatched area C; Fig. 6b). The change in the modeled chemical composition ($X_{Fe}$) of the dolomite (Fig. 6b) is in good agreement with that of the EPM-analyses of the dolomite$_{s.s.2}$ (Table 1, No. 4–8; Fig. 3a). In addition, the measured chemical composition of the magnesite$_{s.s.}$ inclusions ($X_{Fe} \approx 0.47$) in dolomite (Table 1, No. 9–10) corresponds with that of the modeled magnesite$_{s.s.}$ ($X_{Fe} = 0.40–0.50$) in the pseudosection (area B–C; Fig. 6b).

Chemical zoning in metamorphic minerals relates to the changing effective bulk rock composition and the precipitating fluid during changing pressures and/or temperatures (e.g., Tracy 1982). In case of a closed chemical system chemical zoning is directly related to the availability of reactants and the degree of reaction completion. Reaction (3) suggests that dolomite and garnet formed simultaneously. The garnet in eclogite L0910 shows distinctive prograde growth zoning with continuously decreasing Fe- and Mn-contents and a gradually
increasing Mg-content from core to rim, respectively (Li et al. 2013). X-ray maps and composition profiles display that the dolomite porphyroblasts exhibit the same compositional zoning as the garnets (Figs. 2 and 3a). The symmetric concentric chemical zoning occurs both in matrix dolomite and dolomite inclusions in garnet (Fig. 4) suggesting that the zoning is the product of prograde growth processes. This assumption is supported by the following evidence: 1) the dolomite contains mineral inclusions of glaucophane, lawsonite (and its pseudomorphs), chlorite, allanite, epidote, white mica and omphacite (Fig. 1) indicating that the growth of dolomite may have occurred during the blueschist-facies to eclogite-facies stages; 2) the thermodynamic modeling reveals that the Fe substitution of Mg in dolomite decreases during the prograde \( P-T \) evolution (Fig. 6), which is in agreement with the observed Fe–Mg zoning in dolomite; and 3) matrix dolomite grains and dolomite inclusions in garnet have the same core (-mantle) compositional zoning pattern (Fig. 4).

Decreasing Fe and increasing Mg contents from core to rim of the dolomite are believed to be the result of a changing matrix bulk rock composition during temperature increase as revealed by the thermodynamic modeling (Fig. 6). The prograde chlorite and amphibole breakdown supply the Mg for the dolomite formation and at the same time the garnet crystallization reduces the Fe concentration in the system. However, the core–to–inner rim Mn decrease of the dolomite is thought to be the result of fractional crystallization, which was already proposed for similar zoned siderite porphyroblasts from greenschist-facies phyllites of the Esplanade Range and Northern Dogtooth Mountains in British Columbia (Jones and Ghent 1971). Trace element zoning of dolomite such as decreasing core–to–rim concentrations of Sr, Pb, transition metal elements, REE (Fig. 5a–d) and Y (cf., garnet, Hollister 1966), is believed to be further evidence for fractional crystallization of the dolomite. The abrupt Mn increase at the outer-rim of the dolomite accompanied by large compositional changes of the Fe- and Mg-contents (Figs. 2 and 3) along with the sudden
variations of trace elements (Fig. 5a–c), may be attributed to variations in the equilibrium fluid composition or to disequilibrium crystallization during the last porphyroblastic growth stages (cf., Jones and Ghent 1971).

**The occurrence of magnesite in dolomite in the Tianshan eclogites**

The occurrence of magnesite ± calcite (aragonite) inclusions in dolomite was interpreted as evidence for UHP metamorphism in excess of 5 GPa for eclogite-facies-rocks from the Tianshan orogen (Zhang et al. 2002, 2003). These authors referred to the equilibrium reaction dolomite = magnesite + aragonite in order to deduce these exceptionally high UHP conditions (cf., Hammouda et al. 2011, and references therein). The stability of magnesite at ultrahigh pressure conditions (e.g., >5GPa) was confirmed by a series of experiments (Hammouda et al. 2011, and references therein) and some field observations (e.g., Zhang and Liou 1994; Messiga et al. 1999). On the other hand, Fe-rich magnesite$_{c.s.}$ and dolomite$_{c.s.}$ were experimentally shown to be stable at HP as well as UHP conditions in mafic Fe-rich eclogites. However, the influence of Fe on the carbonate structure and thus their stability was not discussed in detail by these studies (e.g., Dasgupta et al. 2004; Yaxley and Brey 2004), although recently it was experimentally shown that the Fe-content plays an decisive role in effecting the ordering-disordering state of dolomite (Franzolin et al. 2012) and, thus, has a considerable effect on the magnesite-aragonite-dolomite stability relationship (Hammouda et al. 2011). In Fe-bearing systems, experimental results suggest that the nucleation of aragonite and magnesite occurs prior to that of dolomite at relatively low-pressure/low-temperature conditions. Furthermore, a relatively high Fe proportion is expected to shift the aragonite + magnesite$_{c.s.}$ ↔ dolomite reaction toward higher temperatures, enlarging the stability field of aragonite and magnesite$_{c.s.}$ (Franzolin et al. 2012). For instance, aragonite and magnesite$_{c.s.}$ are stable between 400 and 450°C at ca. 2 GPa and react to highly disordered dolomite only
at temperatures $> 450^\circ$C in Fe-rich systems (see Fig. 10 in Hammouda et al. 2011). In the present study, the application of a new thermodynamic solid-solution model for Ca–Mg–Fe carbonate provides an opportunity to investigate the transition of carbonate minerals during subduction zone metamorphism. In the modeled complex system using a particular bulk chemistry (Fig. 6a) aragonite occurs in the low temperature/low pressure stability fields in the phase equilibrium diagram while magnesite$_{s.s.}$ appears only at $P > 2.0$ GPa (Fig. 6) indicating that Fe-rich magnesite (in equilibrium with dolomite) is stable under high-pressure conditions ($P \leq 2.5$ GPa, $T \leq 600^\circ$C), but is expected to react out to dolomite at temperatures $> 600^\circ$C (Fig. 6).

Thus, the reported magnesite$_{s.s.}$ inclusions in dolomite$_{s.s.}$ 2 (Table 1) from the Tianshan HP eclogites may have formed prograde in equilibrium with dolomite$_{s.s.}$ 1 and not during decompression as previously proposed (Zhang et al. 2003). This interpretation is also supported by glaucophane inclusions in the magnesite (Fig. 1c) and the occurrence of dolomite-rimmed magnesite inclusions in the core domain of prograde garnet porphyroblasts (Fig. 1a–b) (see also Li et al. 2012). These textural observations indicate that Fe-magnesite formed at the expense of glaucophane between 500 and 560$^\circ$C at $2.0 \leq P \leq 2.3$ GPa and was then transformed to dolomite prior to or simultaneously with the pervasive garnet growth during increasing $P$–$T$ conditions. Consequently caution is warranted in interpreting magnesite occurrences in dolomite in eclogite facies rocks as unambiguous evidence for UHP metamorphism (see also Smit et al. 2008). Alternatively, fluid flow along micro cracks may enter the inner part of garnet (or other container minerals) and thus may change the carbonate composition of inclusions forming pseudomorph after older minerals. In addition, it should be kept in mind that magnesite and dolomite assemblages cannot be treated as an absolute pressure indicator without a strict control of the relative amounts of volatile and non-volatile components in multi-component Fe-bearing systems (Poli et al. 2009).
IMPLICATIONS

Compositionally zoning was observed in dolomite in a lawsonite-bearing eclogite from the western Tianshan HP–UHP metamorphic belt. Evidence from mineral inclusions, thermodynamic modeling and textures suggest the zoning formed during prograde dolomite growth under HP metamorphism. To our knowledge the compositional zoning of carbonate is very rare in metamorphic rocks, and this is the first report showing the possibility to retrieve such a long history from high-pressure carbonates, which are generally believed to record only the latest stages of the metamorphic evolution of eclogite-facies rocks. The core–to–rim Mg–Fe–Mn zoning of dolomite formed contemporaneously with garnet thereby suggesting that the dolomite, like garnet, also experienced fractional crystallization during the HP metamorphism. Therefore more attention should be paid to the carbonates when considering mineral equilibrium and effective bulk-rock composition calculations in HP–UHP carbonate-bearing rocks. In addition, our findings show that the chemical zoning in dolomite is largely temperature dependent and thus the analysis of major and trace elements in carbonates from blueschists and eclogites may bear important thermobarometric implications.

The present study shows that carbonates in subducted oceanic crust may experience gradual aragonite $\rightarrow$ dolomite $\rightarrow$ dolomite+magnesite transition stages during blueschist- to eclogite-facies conditions. The occurrence of magnesite$_{s.s.}$ inclusions in dolomite enclosed in garnet indicates that the magnesite$_{s.s.}$ had formed already under HP conditions. Fe content in magnesite determines its stability at lower pressures. Thus, caution is warranted using magnesite occurrences in eclogite-facies rocks as unambiguous evidence for UHP metamorphism, in particular in a multi-component Fe-bearing system.
ACKNOWLEDGMENTS

This study was funded by the Deutsche Forschungsgemeinschaft (KL692/17-3) and the National Natural Science Foundation of China (41025008). We are grateful to Dr. H. Brätz for assistance with the LA–ICP–MS and to Dr. H.X. Bao for help with the Raman measurements. Dr. T. John is thanked for discussion on various topics of the manuscript. The first author thanks the DAAD for the scholarship supporting his PhD study in Germany. Constructive reviews by Drs. S. Poli and H.P. Schertl are greatly appreciated. Dr. E. Ghent is thanked for his comments and editorial work. This publication is a contribution to IGCP Project 592.

REFERENCES CITED


pyroxenes in the system jadeite-diopside-hedenbergite-acmite, with applications to
eclogite rocks. American Mineralogist, 92, 1181–1189.
Hammouda, T., Andrault, D., Koga, K., Katsura, T., and Martin, A.M. (2011) Ordering in
double carbonates and implications for processes at subduction zones. Contributions to
Mineralogy and Petrology, 161, 439–450.
Han, B.-F., He, G.-Q., Wang, X.-C., and Guo, Z.-J. (2011) Late Carboniferous collision
between the Tarim and Kazakhstan-Yili terranes in the western segment of the South Tian
Shan Orogen, Central Asia, and implications for the Northern Xinjiang, western China.
Earth-Science Reviews, 109, 74–93.
Hollister, L.S. (1966) Garnet Zoning: An Interpretation Based on the Rayleigh Fractionation
in slabs due to non steady-state fluid-rock interaction: Constraints from an eclogite-facies
transport vein in blueschist (Tianshan, China). Lithos, 103, 1–24.
John, T., Gussoni, N., Podladchikov, Y.Y., Bebout, G.E., Dohmen, R., Halama, R., Klemd, R.,
Magna, T., and Seitz, H.-M. (2012) Volcanic arcs fed by rapid pulsed fluid flow through
Jones, J.W. and Ghent, E.D. (1971) Zoned siderite porphyroblasts from the Esplanade range
and northern Dogtooth mountains, British Columbia. American Mineralogist, 56, 1910–
1916.
oceanic metabasalts: implications for seismicity, arc magmatism and volatile recycling.


eclogitic rocks in western Tianshan, northwest China: Convincing proof of UHP
metamorphism. American Mineralogist, 93, 1845–1850.

Tianshan, NW China and its tectonometamorphic implication. Journal of Metamorphic
Geology, 27, 773–787.

magnesiochloritoid eclogites from the Monviso ophiolites (Western Alps, Italy). Journal of
Metamorphic Geology, 17, 287–299.

oceanic crust: an experimental study on H₂O-CO₂-bearing basalts. Earth and Planetary

hydrogen in subducted oceanic crust: An experimental study to 5 GPa. Earth and Planetary

metamorphism in marbles: Phase relations in high-grade aluminous calcite-dolomite
marbles from the Greek Rhodope massif in the system CaO-MgO-Al₂O₃-SiO₂-CO₂ and
indications of prior aragonite. Lithos, 104, 119–130.

Kopp, Eds., Luminescence Microscopy: Quantitative and Qualitative Aspects. SEPM
Short Course Notes, 25, 77–82.


Reinecke, T., Bernhardt, H.J., and Wirth, R. (2000) Compositional zoning of calcite in a high-
pressure metamorphic calc-schist: clues to heterogeneous grain-scale fluid distribution
during exhumation. Contributions to Mineralogy and Petrology, 139, 584–606.


Zhang, L., Ellis, D.J., Arculus, R.J., Jiang, W., and Wei, C. (2003) 'Forbidden zone' subduction of sediments to 150 km depth - the reaction of dolomite to magnesite plus aragonite in the UHPM metapelites from western Tianshan, China. Journal of


**FIGURE CAPTIONS**

**Figure 1** Representative photomicrographs and BSE images of dolomite in carbonate-lawsonite-bearing eclogite in the Tianshan (U)HP/LT metamorphic belt. All=allanite, Cal=calcite, Chl=chlorite, Dol=dolomite, Ep=epidote, Gln=glaucophane, Grt=garnet, Law=lawsonite, Mag$_{s.s.}$=magnesite-siderite$_{s.s.}$, Omp=omphacite, Phn=phengite, Pg=paragonite, Py=pyrite, Qtz=quartz, Ttn=titanite. (a, b) Dolomite inclusions in garnet and coarse-grained matrix dolomite, both enclosing Mag$_{s.s.}$ inclusions. (c) Mag$_{s.s.}$ inclusions in dolomite containing glaucophane inclusions. (d) The zoned porphyroblastic dolomite contains inclusions of calcite, chlorite, phengite, paragonite, allanite and omphacite. The calcite was identified by the representative Raman shifts at 154 cm$^{-1}$, 279 cm$^{-1}$, 713 cm$^{-1}$ and 1085 cm$^{-1}$. (e) Glaucophane inclusions in dolomite. (f) Phengite, allanite/epidote, omphacite and quartz inclusions in matrix dolomite. (g) Lawsonite inclusions and its pseudomorph (epidote+paragonite assemblages) in the core domain of matrix dolomite. (h) Calcite-chlorite-dolomite inclusions in garnet in nearby carbonate-bearing eclogite, see also Fig. 3d from Li et al. (2012).

**Figure 2** X-ray intensity maps of Ca, Fe, Mg and Mn in the dolomite porphyroblast from Fig. 1d. The compositional zoning is displayed by core–to–rim gradually increasing Mg and decreasing Fe and Mn, whereas Ca is rather homogeneous (for profile A–B see Fig. 3a).
numbered circles represent LA–ICP–MS spots, the data of which are listed in Table 2.

**Figure 3** Chemical composition profile of the dolomite porphyroblast from Fig. 2. (a) Fe and Mn decrease from core to rim while Mg increases and Ca is constant. Towards the outermost rim Ca and Mn increase slightly. (b) Good negative correlation of Mg and Fe. (c, d) Mn shows a negative correlation with Mg and a positive correlation with Fe, respectively.

**Figure 4** X-ray maps of Ca, Fe, Mg and Mn of dolomite grains from Fig. 1a–b. The dolomite inclusions in garnet shows the same compositional zoning as the core (-mantle) domain of matrix dolomite.

**Figure 5** Trace elements in the zoned matrix dolomite porphyroblast from Fig. 2 and the magnesite inclusions in dolomite. (a–c) Trace element concentrations along a profile from core to rim in the dolomite. (a) Li–Ba–Sr–Pb. (b) Transition metal elements. (c) REE and Y. (d) Chondrite-normalized rare earth element patterns. The dolomite core contains higher REE contents (especially HREE) contents than the rim. (e) Chondrite-normalized rare earth element patterns of magnesite inclusions in dolomite. Normalization values are after Sun and McDonough (1989).

**Figure 6** (a) $P$–$T$ pseudosection (using Perple_X) in the system NMnCaKFMASCHO for the eclogite based on an effective bulk composition. The pseudosection is contoured for aragonite, dolomite$_{ss}$ and magnesite$_{ss}$ modal abundances (vol.%). (amp = amphibole; arag = aragonite; chl = chlorite; dol = dolomite; ep = epidote; f = fluid; grt = garnet; law = lawsonite; mag = magnesite; omp = omphacite; phn = phengite; q = quartz; rhc = rhodochrosite; zoi = zoisite). For more mineral assemblages see Table 3. (b) The $P$–$T$ path (for details see Li et al. 2012, 2013) indicates that carbonates in subducted oceanic crust undergo the aragonite $\rightarrow$ dolomite $\rightarrow$ dolomite+magnesite transitions during prograde subduction zone metamorphism. The pseudosections are contoured with $X_{Fe}$ isopleths in magnesite$_{ss}$ and dolomite$_{ss}$. The isopleths are largely $T$-dependent in area C: the Fe-content decreases and the Mg-content
increases from low-$T$ to high-$T$, which is in agreement with the measured compositional zoning in eclogite-facies dolomite of this study. (c–g) The contoured modal amounts (vol.%) of chlorite (c), amphibole (d), omphacite (e), lawsonite (f) and garnet (g).
<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>core</td>
<td>mantle</td>
<td>core</td>
<td>mantle</td>
<td>rim</td>
<td>core</td>
<td>mantle</td>
<td>inner-rim</td>
<td>outer-rim</td>
<td>in Dol</td>
<td>in Dol</td>
<td>in Dol</td>
<td>matrix</td>
<td>in Dol</td>
<td>in Dol</td>
<td>in Grt</td>
<td>in Dol</td>
<td>in Grt</td>
<td>in Mag</td>
<td>matrix</td>
<td>in Dol</td>
<td>in Dol</td>
<td>in Dol</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>35.01</td>
<td>37.64</td>
<td>37.33</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.07</td>
<td>56.69</td>
<td>55.87</td>
<td>56.53</td>
<td>53.06</td>
<td>53.52</td>
<td>46.83</td>
<td>39.20</td>
<td>38.88</td>
<td>34.20</td>
<td>38.82</td>
<td>26.18</td>
<td></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.09</td>
<td>0.03</td>
<td>0.03</td>
<td>0.00</td>
<td>0.05</td>
<td>0.03</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
<td>0.49</td>
<td>0.26</td>
<td>0.18</td>
<td>0.04</td>
<td>0.44</td>
<td>0.00</td>
<td>0.12</td>
<td>0.48</td>
<td>0.00</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>23.13</td>
<td>21.58</td>
<td>21.99</td>
<td>0.04</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>10.72</td>
<td>10.03</td>
<td>11.19</td>
<td>10.32</td>
<td>26.38</td>
<td>25.57</td>
<td>39.23</td>
<td>26.35</td>
<td>28.58</td>
<td>20.21</td>
<td>30.76</td>
<td>18.53</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.11</td>
<td>0.07</td>
<td>0.08</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.09</td>
<td>0.01</td>
<td>0.16</td>
<td>0.07</td>
<td>0.07</td>
<td>0.01</td>
<td>0.13</td>
<td>0.02</td>
<td>0.12</td>
<td>0.00</td>
<td>0.16</td>
</tr>
<tr>
<td>FeO</td>
<td>29.68</td>
<td>29.84</td>
<td>27.10</td>
<td>12.66</td>
<td>11.69</td>
<td>10.02</td>
<td>9.57</td>
<td>7.51</td>
<td>34.32</td>
<td>33.40</td>
<td>1.93</td>
<td>7.81</td>
<td>9.50</td>
<td>12.79</td>
<td>11.94</td>
<td>2.31</td>
<td>3.18</td>
<td>0.45</td>
<td>8.25</td>
<td>5.11</td>
<td>11.89</td>
<td>0.79</td>
<td>29.99</td>
</tr>
<tr>
<td>MnO</td>
<td>1.87</td>
<td>1.72</td>
<td>0.73</td>
<td>0.53</td>
<td>0.38</td>
<td>0.26</td>
<td>0.15</td>
<td>0.40</td>
<td>0.54</td>
<td>1.36</td>
<td>0.40</td>
<td>0.07</td>
<td>0.02</td>
<td>0.01</td>
<td>0.08</td>
<td>0.02</td>
<td>0.03</td>
<td>0.00</td>
<td>0.15</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.25</td>
</tr>
<tr>
<td>MgO</td>
<td>1.22</td>
<td>2.23</td>
<td>2.91</td>
<td>13.29</td>
<td>14.14</td>
<td>15.29</td>
<td>16.97</td>
<td>21.35</td>
<td>20.71</td>
<td>0.95</td>
<td>5.98</td>
<td>5.40</td>
<td>8.64</td>
<td>9.64</td>
<td>3.66</td>
<td>3.62</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09</td>
<td>0.20</td>
<td>0.01</td>
<td>13.29</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>8.80</td>
<td>7.82</td>
<td>9.87</td>
<td>27.67</td>
<td>28.60</td>
<td>28.84</td>
<td>28.88</td>
<td>30.38</td>
<td>0.59</td>
<td>0.67</td>
<td>59.24</td>
<td>10.93</td>
<td>9.53</td>
<td>1.15</td>
<td>0.72</td>
<td>0.05</td>
<td>0.06</td>
<td>1.19</td>
<td>22.89</td>
<td>23.86</td>
<td>17.62</td>
<td>17.41</td>
<td>0.05</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>8.43</td>
<td>9.35</td>
<td>7.18</td>
<td>7.47</td>
<td>0.00</td>
<td>0.01</td>
<td>0.08</td>
<td>0.03</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.02</td>
<td>0.00</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>10.23</td>
<td>10.48</td>
<td>0.84</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>99.95</td>
<td>100.95</td>
<td>100.05</td>
<td>54.22</td>
<td>54.90</td>
<td>54.74</td>
<td>53.98</td>
<td>55.33</td>
<td>56.83</td>
<td>56.16</td>
<td>62.71</td>
<td>100.83</td>
<td>99.83</td>
<td>96.68</td>
<td>97.20</td>
<td>112.66</td>
<td>97.00</td>
<td>95.16</td>
<td>97.53</td>
<td>96.65</td>
<td>84.45</td>
<td>88.27</td>
<td>88.48</td>
</tr>
</tbody>
</table>

Representative major element composition of minerals in dolomite-bearing eclogite

(i) X\(_Fe\) = Fe\(^{2+}\)/(Fe\(^{2+}\)+Mg); Alm: almandine, Grs: grossular, Prp: pyrope, Sp: spessartine, WEF: wollastonite+enstatite+ferrosilite, JD: jadeite, AE: aegirine, Ps: pistacite. (ii) Fe\(^{3+}\) was calculated assuming stoichiometric mineral compositions.
Table 2
Representative trace element composition (in ppm) of dolomite and magnesite. Analyses 1-15 refer to the profile in dolomite (Fig. 2 Mn).

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Magnesite</th>
<th>Dolomite</th>
<th>Core</th>
<th>Rim</th>
<th>in matrix Dol</th>
<th>Dol/Gt</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>2.26</td>
<td>2.14</td>
<td>2.14</td>
<td>2.51</td>
<td>1.75</td>
<td>1.21</td>
</tr>
<tr>
<td>P</td>
<td>28.4</td>
<td>27.7</td>
<td>24.8</td>
<td>26.8</td>
<td>22.6</td>
<td>22.5</td>
</tr>
<tr>
<td>Si</td>
<td>bdl</td>
<td>bdl</td>
<td>365</td>
<td>bdl</td>
<td>bdl</td>
<td>433</td>
</tr>
<tr>
<td>Ti</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>252</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>V</td>
<td>2.35</td>
<td>2.13</td>
<td>2.17</td>
<td>1.87</td>
<td>1.88</td>
<td>1.63</td>
</tr>
<tr>
<td>Cr</td>
<td>5.29</td>
<td>5.16</td>
<td>5.33</td>
<td>2.92</td>
<td>2.45</td>
<td>4.73</td>
</tr>
<tr>
<td>Mn</td>
<td>3993</td>
<td>3646</td>
<td>3763</td>
<td>3538</td>
<td>3021</td>
<td>2824</td>
</tr>
<tr>
<td>Zn</td>
<td>132</td>
<td>132</td>
<td>130</td>
<td>130</td>
<td>132</td>
<td>134</td>
</tr>
<tr>
<td>Rb</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Sr</td>
<td>1275</td>
<td>1280</td>
<td>1344</td>
<td>1305</td>
<td>1274</td>
<td>1224</td>
</tr>
<tr>
<td>Y</td>
<td>10.9</td>
<td>6.36</td>
<td>4.27</td>
<td>1.63</td>
<td>1.28</td>
<td>0.757</td>
</tr>
<tr>
<td>Zr</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Nb</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Mo</td>
<td>0.135</td>
<td>0.225</td>
<td>0.161</td>
<td>0.107</td>
<td>0.093</td>
<td>0.076</td>
</tr>
<tr>
<td>Cs</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Ba</td>
<td>1.90</td>
<td>1.95</td>
<td>2.19</td>
<td>1.87</td>
<td>2.50</td>
<td>1.63</td>
</tr>
<tr>
<td>La</td>
<td>0.316</td>
<td>0.252</td>
<td>0.239</td>
<td>0.100</td>
<td>0.121</td>
<td>0.317</td>
</tr>
<tr>
<td>Ce</td>
<td>1.05</td>
<td>0.690</td>
<td>0.733</td>
<td>0.330</td>
<td>0.385</td>
<td>0.738</td>
</tr>
<tr>
<td>Pr</td>
<td>0.174</td>
<td>0.140</td>
<td>0.138</td>
<td>0.066</td>
<td>0.088</td>
<td>0.107</td>
</tr>
<tr>
<td>Nd</td>
<td>1.51</td>
<td>1.06</td>
<td>1.08</td>
<td>0.493</td>
<td>0.375</td>
<td>0.787</td>
</tr>
<tr>
<td>Sm</td>
<td>0.711</td>
<td>0.687</td>
<td>0.661</td>
<td>0.266</td>
<td>0.252</td>
<td>0.259</td>
</tr>
<tr>
<td>Eu</td>
<td>0.596</td>
<td>0.458</td>
<td>0.473</td>
<td>0.483</td>
<td>0.442</td>
<td>0.381</td>
</tr>
<tr>
<td>Gd</td>
<td>2.14</td>
<td>1.40</td>
<td>1.29</td>
<td>0.445</td>
<td>0.721</td>
<td>0.447</td>
</tr>
<tr>
<td>Tb</td>
<td>0.381</td>
<td>0.256</td>
<td>0.208</td>
<td>0.086</td>
<td>0.068</td>
<td>0.066</td>
</tr>
<tr>
<td>Dy</td>
<td>2.39</td>
<td>1.66</td>
<td>1.14</td>
<td>0.410</td>
<td>0.287</td>
<td>0.249</td>
</tr>
<tr>
<td>Ho</td>
<td>0.418</td>
<td>0.257</td>
<td>0.135</td>
<td>0.080</td>
<td>0.043</td>
<td>0.028</td>
</tr>
<tr>
<td>Er</td>
<td>0.769</td>
<td>0.390</td>
<td>0.273</td>
<td>0.105</td>
<td>0.097</td>
<td>0.041</td>
</tr>
<tr>
<td>Tm</td>
<td>0.070</td>
<td>0.055</td>
<td>0.030</td>
<td>0.014</td>
<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td>Yb</td>
<td>0.463</td>
<td>0.323</td>
<td>0.173</td>
<td>0.055</td>
<td>0.027</td>
<td>0.039</td>
</tr>
<tr>
<td>Lu</td>
<td>0.035</td>
<td>0.049</td>
<td>0.026</td>
<td>0.012</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Hf</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>0.259</td>
<td>0.149</td>
<td>0.171</td>
</tr>
<tr>
<td>Ta</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Pb</td>
<td>16.4</td>
<td>16.6</td>
<td>17.4</td>
<td>17.0</td>
<td>15.9</td>
<td>16.2</td>
</tr>
<tr>
<td>Th</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>U</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
</tbody>
</table>

*bdl: below detection limit; Dol/Gt: magnesite in dolomite in garnet.
<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>MnO</th>
<th>CO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>L0910</td>
<td>43.39</td>
<td>12.71</td>
<td>3.44</td>
<td>1.19</td>
<td>7.24</td>
<td>1.9</td>
<td>6.73</td>
<td>12.76</td>
<td>0.11</td>
<td>5.77</td>
<td>4.68</td>
</tr>
</tbody>
</table>

Field A:

- A₁: amp gnp grt phn chl arag law q f
- A₂: amp gnp grt phn chl dol arag law q f
- A₃: amp gnp grt phn chl dol arag law f

Field B:

- B₁: amp gnp grt phn chl dol law f
- B₂: gmp gnp grt phn chl dol mag law f
- B₃: gmp gnp grt phn dol mag law f
- B₄: gmp gnp grt phn dol mag law f q

Field C:

- C₁: gnp grt phn dol mag law q f
- C₂: gnp grt phn dol mag law q f
- C₃: gnp grt phn dol mag ep q f

Table 3: Bulk composition used for pseudosection calculation and mineral assemblages from Fig. 6a

A: gnp phn chl amp dol mag law rhc f
B: amp gnp phn chl dol law arag rhc f
C: amp gnp phn chl arag law ep q f
D: amp gnp phn chl dol arag law ep q f
E: amp gnp phn chl dol arag law ep f
F: amp gnp phn chl arag ep q f
G: amp gnp phn chl dol arag ep q f
H: amp gnp phn chl dol arag ep f
I: amp gnp phn dol law f
J: amp gnp phn dol law ep f
K: amp gnp phn dol law ep q f
L: amp gnp phn dol mag law ep q f
M: amp gnp phn dol mag ep q f
N: amp gnp phn dol law q f
O: amp gnp phn dol zoi q f
Figure 4
Figure 5
Figure 6