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PETROGRAPHIC, MINERAL CHEMICAL CHARACTERISTICS AND ROLE OF MARBLES IN FORMATION OF GEM DEPOSITS IN LUC YEN-YEN BAI PROVINCE, NORTHERN VIETNAM

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ABSTRACT

Gem deposits in Luc Yen such as ruby, sapphire and spinel discovered in Khoan Thong – An Phu, Lo – Gam Structural Zone have been considered a gemstone supply for domestic and international markets. The gemstone formation in the region has mainly been associated with marble and metamorphism. Based on petrographic and chemical characteristics, the marble in the region was subdivided into three main groups: corundum-bearing (ruby, sapphire) marble, spinel-bearing marble and non-gemstone bearing marble. Although all of these marble groups demonstrate the same petrographic properties, they have likely been metamorphosed from inhomogeneous Al-, Mg-rich primary rocks. The difference in Al and Mg content in the primary rocks may have led to concentration of gemstone in the aforementioned marble groups under intermediate – high P-T conditions. The result from P-T-XCO_2 shows that gemstone-bearing marble has been resulted from regional metamorphism, belonging to the upper part of the Amphibolite facies and the lower part of the Granulite Facies (T = 700 - 750^{o}C).

1. GEOLOGIC SETTINGS AND GEM DEPOSITS

Deposits of gem corundum (Crn) (mainly ruby) and spinel (Spl) in Luc Yen - Yen Bai province (North Vietnam) in the Lo - Gam zone occur in a thick metasedimentary sequence of Upper Proterozoic–Lower Cambrian age, composed of marble and overlying sillimanite (Sli) – biotite (Bt)-garnet (Grt) schist (Pham Van Long et al., 2004). These units, bounded by left-lateral faults, are intruded by granitic rocks and related pegmatites of Triassic age (Phan Trong Trinh et al., 1997).

2. RESULTS

2.1. Petrographic characteristics of gem-bearing marbles

Corundum-bearing marble: Commonly contains calcite (Cal) with corundum revealing pink to red colors which may be called as pink sapphire and ruby. Apart from calcite and corundum, amphibole (Am), phlogopite (Phl), and pyrrhotite (Pyr) are also found in this marble. In addition, graphite (Grap), rutile, sphene, muscovite (Mus), margarite (Mar), chlorite, pyrite, spinel, feldspar and clinochlore can also be found in some samples. Corundum has various sizes between 1 and 4 mm.

Typical mineral paragenesis recognized for corundum-bearing marbles is Cal + Crn ± Am ± Phl ± Mar ± Mus ± Grap ± Pyr ± feldspar (anorthite) ± chlorite ± pyrite.

Spinel-bearing marble: Dominant calcite (and dolomite) in association with red to purple coloured spinel, green to greenish amphibole, clinohumite (Chu), forsterite, phlogopite, pyrrhotite and chlorite. Other minerals such as clinochlore, margarite, muscovite, feldspar (anorthite), and graphite are also found in some samples. Moreover, sphene, apatite and zircon can be found as accessory minerals. Spinel is mostly red to pink, usually form distorted euhedral crystals which seem to have been affected from high pressure. They vary in size from about 2 to 5 mm. Calcites and dolomites observed in this group are more turbid crystals comparing to the other groups.

Spinel-bearing marbles are characterized by the next two mineral parageneses: (a) Cal + Do + Spl + Par ± Phl ± Grap; (b) Cal + Dol + Spl ± Chu + forsterite + chlorite ± Grap ± Par ± Phl ± clinozoisite ± feldspar (anorthite) ± Crn.

Gem-free marble: Both corundum and spinel are absent in this marble group although phlogopite (+Am?), pyrrhotite and rutile still exist. Pyrrhotite and rutile have similar sizes (av. 0.5-1 mm) to those present in the previous groups. Phlogopite has typical lepidoblastic tecture.

Gem-bearing marbles from Yen Bai were analyzed for major and trace elements in order to determine possible sources of the chemical elements (Al, Mg, Cr, V, Ga, etc.) in corundum (ruby) and spinel.

2.2. Chemical characteristics of minerals

Calcite: Although, calcites, the dominant composition in all marble groups, have similar main Ca composition, their trace compositions are somehow different. Calcites in corundum-bearing and gem-free marbles are almost pure Ca composition whereas those in spinel-bearing one show Mg-richer composition as shown in the plots of atomic Ca-Fe-Mg proportion. Regarding to atomic trace composition, most calcites coexisting with spinel yield consistently high Mg against Mn and Fe. On the other hand, calcites in corundum-bearing and gem-free marbles usually vary between Fe and Mn sites, although a few analyses appear on the Mg site.

Corundum and spinel: Corundum is likely pure Al_2O_3 which Al proportion almost reaches 2 atoms/3 oxygen atoms; just 0.002 atoms belong to Cr and Fe. This is typical characteristic of pink sapphire and ruby from Luc Yen and some metamorphic ruby from elsewhere. Spinel yield about 71% Al_2O_3, 27%MgO and 1% FeO with very small amounts of the other elements including Cr_2O_3 and ZnO that indicate almost pure (sensu strictu) spinel endmember and Cr is cause of red to pink color.

Amphibole show quite different properties in corundum - and spinel bearing marbles which is worth of our more detailed investigation.

Other minerals: Similar to amphibole, phlogopite, and sphene have significant amounts of fluorine in their crystal structure.

2.3. Petrology and P-T-X_{CO2} conditions of metamorphism

The mineral rich spinel-clinohumite-pargasite-forsterite±chlinochlor-calcite-dolomite assemblages are well suited to estimate metamorphic T-X_{CO_2} conditions. The phase diagrams in Fig. 1 were calculated with the internally consistent thermodynamic database of Holland and Powell 1998 and updates. Activity corrections for solid solutions in minerals have been applied according to the activity models given by Holland and Powell 1998. The mineral assemblage clinohumite (Chu) - calcite (Cal)-forsterite (Fo)-dolomite (Dol)-spinel (Spl) represents peak metamorphic conditions. A minimum temperature of about 700°C is obtained from Fig. 1 (right). The composition of the involved fluid phase is constrained by the reaction Chu + Chl = Spl + Fo + H_2O in sample AP1 (Fig. 1, left) and Chu + Cal + CO_2 = Fo + Dol + H_2O in sample V1 (Fig.1, right), which is found to be on the water rich fluid side of the diagrams

(XCO_2 <0.3 and 0.12, respectively). Corundum is not present in the dolomite bearing samples. During prograde metamorphism corundum is replaced by spinel through reaction $CaMg(CO_3)_2 + Al_2O_3 \rightarrow MgAl_2O_4 + CaCO_3 + CO_2$.

3. DISCUSSION AND CONCLUSIONS

In this study, Yen Bai marble samples can be separated into three groups, i.e., corundum-bearing, spinel-bearing and gem-free marbles. All marble groups have similar metamorphic textures (medium - to coarse-grained and granoblastic). These textures and distorted spinel, only in spinel-bearing one, appear to have developed under medium to high pressure. Their mineral assemblages contain identically dominant calcite with accessory phlogopite, amphibole and pyrrhotite but some crucial phases, particularly corundum and spinel, are different. In general corundum and spinel are not coexisting in the samples, besides spinels are often found associated with green pargasite amphibole, phlogopite, and forsterite, clinohumite whereas corundum is more closely related to brown aluminopargasites and aluminomagnesiosadanagaite amphibole, phlogopite and margarite. This evidence may indicate Mg-richer and Al-poorer component of the spinel-bearing marble than the corundum-bearing one. Mg-richer calcite and its turbid feature found in spinel-bearing marble can be used to confirm such interpretation. Gem-free marble seems to have lower Mg and Al than the former groups.

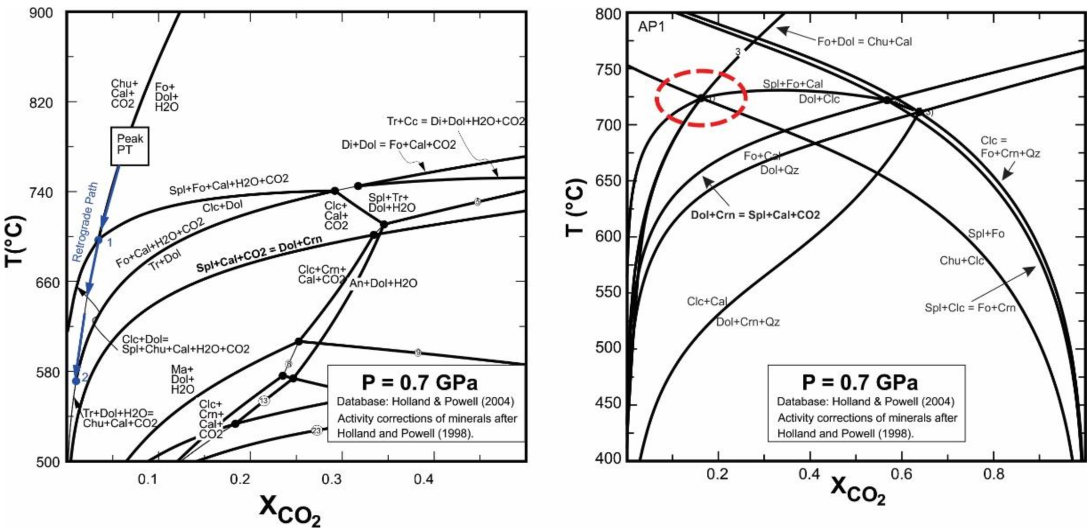

Figure 1. T-XCO_2 diagrams from two spinel-clinohumite-pargasite-chlinochlor-forsterite-calcite-dolomite marbles. Temperature can be estimated with 700-750°C and mineral assemblages are only stable at water rich fluid composition. Pressure was estimated from a garnet-sillimanite metapelite which was collected nearby

Typical mineral assemblages of gem-bearing marbles in Yen Bai are (Sutthirat et al., 2008; Hauzenberger et al., 2014): (a) Cal + Crn ± brown magnesiosadanagaite/pargasite/hornblende ± Phl ± Mar ± Gra ± Pyr for corundum-bearing marbles; (b) Calcite + dolomite + spinel + chromian pargasite ± phlogopite ± graphite, and (c)Cal + Dol + Spl ± Chu + forsterite + chlorite ± Grap ± Par ± Phl ± clinozoisite for spinel-bearing marbles.

These parageneses are essentially similar to those found in marbles from other marble-hosted corundum deposits in Central and South-east Asia (Giuliani et al., 2000, 2007; Garnier, 2003; Garnier et al., 2008). Calcites in corundum-bearing marbles are almost pure Ca composition whereas those in spinel-bearing ones show Mg-richer composition, and both marble groups contain Al, Cr, and V in quantities that are sufficient to form corundum (ruby) and spinel with their typical, red to pink, color. This quite corresponds to the results obtained by previous researchers (Garnier, 2003; Garnier et al., 2008).

Amphiboles in corundum-bearing marbles have quite different properties from those found in spinel-bearing ones, and accordingly, brown magnesiosadanagaite amphiboles can be considered as indicator mineral of corundum-bearing marbles, and green fluorian pargasite amphiboles as indicator mineral of spinel-bearing marbles. Moreover, clinohumite and olivin (forsterite) are found only in spinel-bearing marbles.

Interesting to note that coexisting with corundum and spinel minerals (amphibole, sphen, phlogopite, clinohumite, chlorite) contain noticeable amounts of F, and besides, amphibole also have high alkalis. This supports the idea of contribution of the evaporites to the formation of corundum in marbles (Giuliani et al., 2007; Garnier 2003; Garnier et al., 2008).

Corundum appears not to be present in the dolomite bearing samples. In many samples, especially those collected from Day Nui Con Voi range (Nguyen Ngoc Khoi et al., 2016b), corundum are often surrounded by spinel rim.

These unusual assemblages, mineral inclusions in corundum core and spinel rim, and their chemistry (Nguyen Ngoc Khoi et al., 2016b), and P-T calculation (Fig. 1 above) lead to the proposal that during prograde metamorphism corundum is replaced by spinel through reaction $CaMg(CO_3)_2 + Al_2O_3 \rightarrow MgAl_2O_4 + CaCO_3 + CO_2$. This conclusion is different to that proposed by Garnier et al. (2008) where corundum seems to form from spinel during retrograde metamorphism according to reaction $MgAl_2O_4 + CaCO_3 + CO_2 \rightarrow CaMg(CO_3)_2 + Al_2O_3$. To our awareness, this needs further study and interpretation.

In conclusion, these marbles with different initial components which impure limestone is mostly likely the case, may have been undertaken medium to high grade metamorphism yielding slightly different in mineral assemblages. This agrees well with the previous studies suggested that corundum deposits around the Yen Bai area appear to have been related to moderate to high temperature metamorphism of marble units in the Red River shear zone (Hoang et al., 1999; Garnier, 2003; Pham Van Long, 2003).

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