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Origin and formation of gem quality corundum from Vietnam

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Introduction

Some of the world's most productive gemstone provinces are located in Southeast Asia (De Maesschalck and Oen, 1989, Kane et al., 1992; Galibert et al., 1995; Kane, 1999; Hoang Quang Vinh et al., 1999; Larson, 1999; Phan Trong Trinh et al., 1999; Pecher et al., 2001, Baumgartner et al., 2001; Hauzenberger et al., 2001). A wide variety of gemstones is found in these deposits, mainly varieties of corundum, chrysoberyl, spinel, garnet, beryl, tourmaline, topaz, and zircon. A high consumer demand for precious stones has increased the number of places where gems are mined in the last 30 - 40 years. Identification of the places of origin of gemstones is important to the jewellery industry. However, information on the origin of a gem seldom accompanies a stone from the mine to the stone cutting, jewellery manufacturing and retail sale. Gemmological methods, careful visual classification including growth features, mineral and fluid inclusions as well as mineral properties as colour, brightness and refractory index may be sufficient for an allocation of the gem, but frequently they are not. Geochemical analyses of gem stones provide additional information. Therefore, by applying gemmological and geochemical methods, a gem stone of unknown provenance can be assigned with great certainty to its place of origin. To be able to do that, each gem stone deposit has to be characterized.

Next to assignment of provenance, the geologigal process of formation of primary deposits are of gemmological, economic and scientific interest. They are responsible for the development of all the characteristic diagnostic features mentioned above, and also for the quality of the rough corundum crystals (in all its aspects), prior to reworking during sedimentary processes. These two aspects will be dealt with in this abstract, which focuses on gem quality corundum from Vietnam. Ruby and sapphire are some of the most valued gems. Major producers are Sri Lanka, India, Myanmar, Cambodia, Thailand, Vietnam, Australia, Kenya, Tanzania, and Madagascar.

Only a few geological/mineralogical settings are favorable for the primary formation (crystallization) of corundum because corundum is a relatively rare oxide, which is only stable in quartz-absent, aluminium rich rocks at elevated temperatures and pressures. Principally four different types of *in-situ* corundum deposits are known. These are:

(1) Corundum mineralization associated with metasomatic/metamorphic processes in high grade rocks

(2) Corundum from marbles
(3) Corundum (sapphire) from volcanic rocks
(4) Corundum from pegmatite-like rocks in a feldspathic matrix

However, gem corundum is extracted commercially mainly from secondary deposits. In some cases the primary source of secondary deposits can be guessed. An example are the paleo--alluvial deposits of sapphire in eastern Australia, Thailand and eastern China, which are related to the primary occurrence of sapphire in basalts (Guo et al., 1996, Sutthirat et al., 2001). Guo et al., 1996; Sutherland et al., 1998; and Sutthirat et al., 2001 describe possible mechanisms of formation of sapphire found in basalts. Sutthirat et al., 2001 compared the trace element composition of sapphire found *in-situ* with sapphires from the nearby secondary deposits. The composition of corundum from the *in-situ* samples falls in the range of the analysed values from rubies and sapphires from the alluvial deposit. They conclude that both corundum crystals may be of the same origin.

One type of metamorphic corundum deposit is associated with marbles. The famous Burmese rubies (Mogok) belong to this type. Vietnamese rubies, which have been discovered about 15-20 years ago, are mined commercially at only two localities in Northern Vietnam (Yen Bai and Quy Chau). Both occurrences are secondary alluvial deposits. The primary sources of these rubies are uncertain, but most probably marbles, as one primary occurrence of ruby has been reported in North Vietnam. In Luc Yen, province Yen Bai, pieces of marble with abundant red corundum, which is not of gem quality, can be bought at the local market there. Only little is known about the geology and petrology of the location, where these hand specimens come from. Calcsilicate rocks, allegedly occurring together with the corundum bearing marbles, allow to determine granulite facies conditions of formation (Hauzenberger et al., 2001).

Ruby deposits in Vietnam

Northern Vietnam is an important gem stone producing area in Southeast Asia. Especially the areas around Yen Bai, Province Yen Bai and Quy Chau, Province Nghe An, have reported important gem stone deposits (alluvial deposits). The geological situation and the occurrence of the primary gem stone deposits is not well known. To the north of Yen Bai, close to the city of Luc Yen, marble hosted primary corundum deposits have been reported. Preliminary work has been conducted on a few hand specimens from Luc Yen and on single ruby crystals from Yen Bai and Quy Chau. The ruby concentrates from both mines were provided by the state owned VIGEGO (Vietnam Gem and Gold Cooperation).

Geological Setting

The northern part of Vietnam consists of Precambrian metamorphic rocks, Proterozoic to late Cenozoic magmatic rocks, and Paleozoic to Quarternary sedimentary and volcano-sedimentary rocks (Tran Duc Luong and Nguyen Xuan Bao 1986). Metamorphic rocks comprise weakly metamorphosed quartz-sericite schists, quartzites, and marbles, medium grade kyanite-sillimanite bearing micaschists, gneisses, and garnet amphibolites, and granulite facies rocks. Mafic granulites, calcsilicates, and migmatites indicate temperatures around 800°C and pressures of about 10 kbar (Tran Duc Luong and Nguyen Xuan Bao 1986). A large shear zone, the Ailao Shan - Red River shear zone is a dominant structure in North Vietnam (Fig. 1). It forms a narrow band (10-15 km width, 300 km length) that consists mainly of mylonitic gneisses. K/Ar, Ar/Ar, and U/Pb ages indicate ages of 80 - 29 Ma, much younger than the Precambrian ages given in the geological map of Vietnam (Leloup et al. 1995). Primary corundum is related to granulite facies marbles.

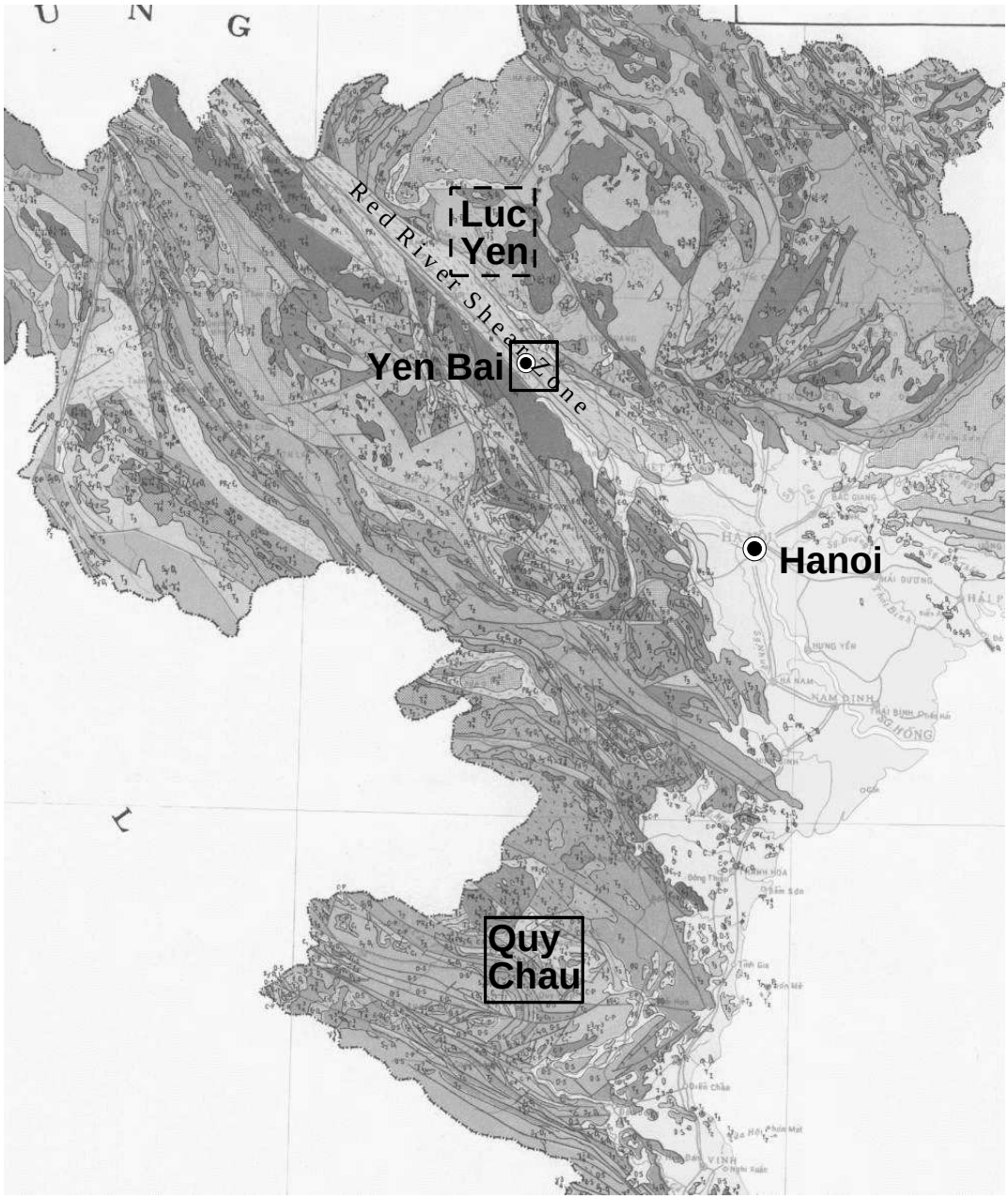


Figure 1: Geological map of N-Vietnam (Tran Duc Luong and Nguyen Xuen Bao, 1986). The solid boxes indicate the gem producing areas of Yen Bai, and Quy Chau. The stippled box indicates the marble hosted corundum occurrence around Luc Yen. Legend: light yellow: neogene sediments; red: intrusive rocks; pink, green, orange and brown: metamorphic basement; blue: limestone and marble

Metapelites, corundum and spinel bearing rocks

Three samples have been collected, two marble/calcsilicate rocks from the same locality in NE-Vietnam, around Luc Yen, one metapelitic sample from the Yen Bai ruby mine (VGS1): (1) a ruby bearing amphibole - phlogopite - sphene - calcite marble (VC1); (2) a spinel bearing clinohumite - forsterite - amphibole - chlorite - phlogopite - dolomite - calcite marble (V1); and a garnet - sillimanite - biotite - plagioclase - K-feldpar and quartz bearing metapelite (VGS1).
(1) Sample VC1 consists mainly of red corundum (ruby), amphibole, phlogopite, some sphene, and calcite. Sphene, phlogopite, and amphibole have significant amounts of fluorine in their crystal

structure. Amphiboles have high Al_2O_3 (21.5 - 22.3 wt.%), high alkalis (Na_2O 3 wt.%, K_2O around 1 wt.%) and high F (1.2 - 1.5 wt.%) contents. They can be classified as aluminopargasites and aluminomagnesiosadanagaites. Nearly a quarter of phlogopite is replaced by its F - bearing variety (F content 1.85 - 2.2 wt.%). Sphene has an Al_2O_3 content of 3.8 wt.% and F values of around 1.2 wt.%. Calcite contains about 1.3 wt.% MgO.

(2) Sample V1 consists of purple spinel, forsterite, clinohumite, amphibole, phlogopite, and chlorite Purple spinel contains only minor amounts of Cr_2O_3 (< 0.34 wt.%) and FeO (< 1.13 wt.%). Olivine is nearly pure endmember forsterite with FeO < 1 wt.% (X_{Mg} > 0.99). Clinohumite, amphibole, and chlorite have high F values. Clinohumite has TiO_2 values of 3.1 - 3.6 wt.%, high F values of 2 - 2.6 wt.% and X_{Mg} > 0.99. Amphiboles contain Al_2O_3 (11.9 - 14.2 wt.%), high Na_2O (1.9 - 2.4 wt.%) and high F (1.2 - 1.5 wt.%) values. They are classified as pargasite, tschermakite, and magnesiohornblende.

(3) The mineral assemblage of sample VGS1 consists of garnet, sillimanite, biotite, plagioclase, K-feldpar and quartz. Muscovite occurs only as retrograde phase typically within or at the rims of K-feldspar. Myrmekitic textures indicate that some melt was present during the peak of metamorphism. Garnet is almandine rich with X_{Alm} = 0.6 at the core and X_{Alm} = 0.7 at the rim. Grossular and spessartine content are below 5 mole %. Biotite contains about 2-3 wt. % TiO_2 and has a X_{Mg} of 0.55-0.65. K-feldspar has about 15-20 mole % albite component. The composition of plagioclase is very homogeneous with X_{Ab} = 0.64. Geothermobarometric calculations (garnet-biotite thermometer, garnet-sillimanite-plagioclase-quartz baromter) yield metamorphic peak conditions of 740-770 °C and 8-10 kbar.

Phase Petrology

The mineral rich assemblage from sample V1 is well suited to estimate metamorphic T - X_{CO_2} conditions. The phase diagram in Figure 2 was calculated with the internally consistent thermodynamic database of Holland and Powell 1998. 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 (Chum) - calcite (Cc) - forsterite (Fo) - dolomite (Dol) - spinel (Sp) represents peak metamorphic conditions. A minimum temperature of about 700°C is obtained from Figure 2. Leloup et. al. 1995 reported P - T estimates for the Day Nui Con Voi metamorphic belt of 780°C and about 7 kbar. The composition of the involved fluid phase is constrained by the reaction Chum + Cc + CO_2 = Fo + Dol + H_2O, which is found to be on the water rich fluid side of the diagram (X_{CO_2} < 0.12). Corundum is not present in the dolomite bearing sample V1. During prograde metamorphism Cor + Dol is replaced by Sp + Cc (Figure 2).

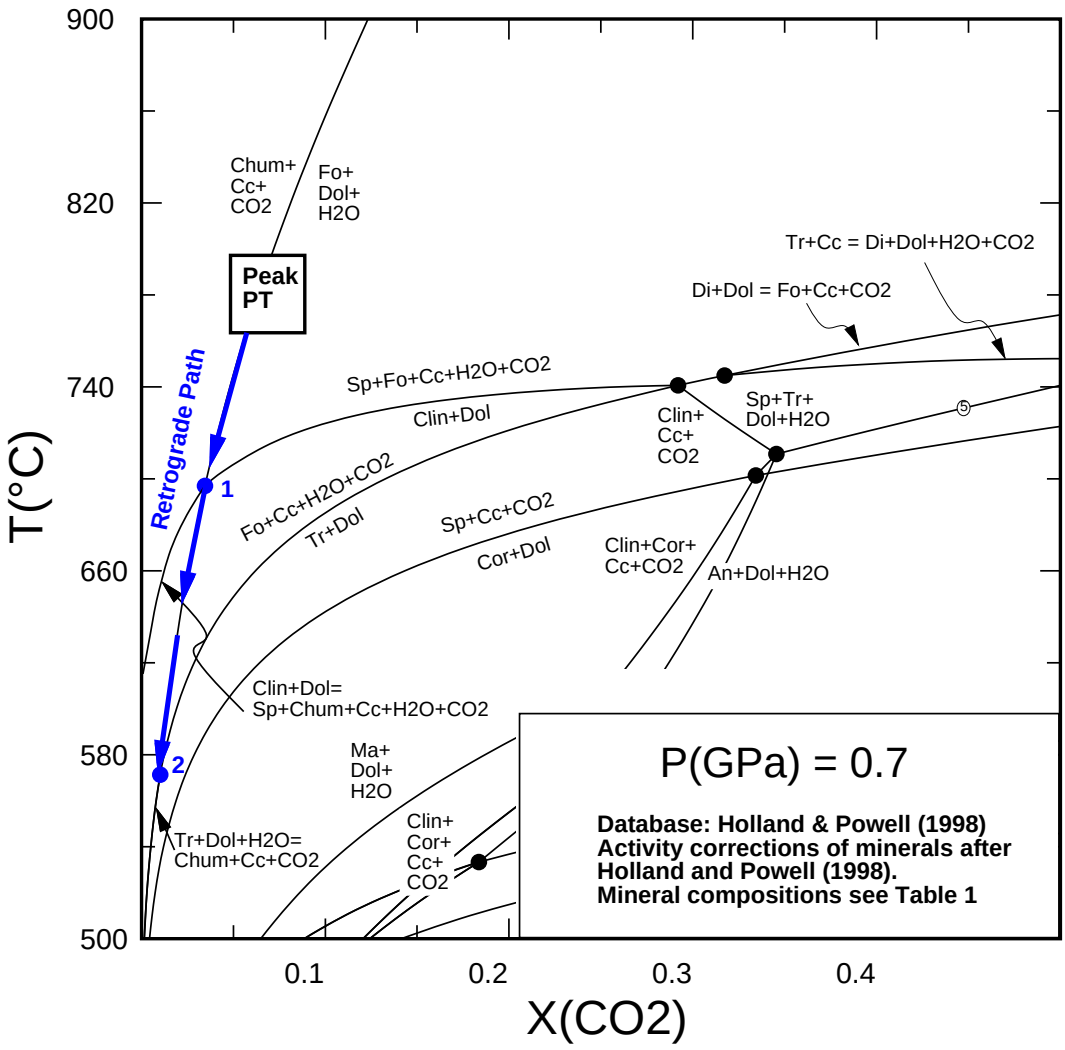


Figure 2: T - X_{CO_2} diagram of Sp-Chum-Fo-Phl-Chl-Cc-Dol calcsilicate rocks. Peak PT estimates are taken from Leloup et al. 1995.

Stable Isotope Chemistry

Stable isotopes of oxygen and carbon have been analysed for individual minerals in sample VC1 and V1. The high values of delta ^{18}O of corundum (22.42) in sample VC1 clearly indicates that this mineral was formed by metamorphic reactions within the marble. The oxygen (25.65 - 26.15) and carbon isotope (1.53 - 2.03) signature of calcite show typical sedimentary signature. Hence no significant metasomatism is indicated by the isotope data. Silicates from sample V1 have lower delta ^{18}O values indicating some interaction with fluids from neighbouring magmatic or metamorphic rocks. Clinohumite has delta ^{18}O of 13.03, chlorite delta ^{18}O of 15.05, spinel of delta ^{18}O 14.34, forsterite delta ^{18}O of 14.32, and amphibole has a delta ^{18}O of 15.05.

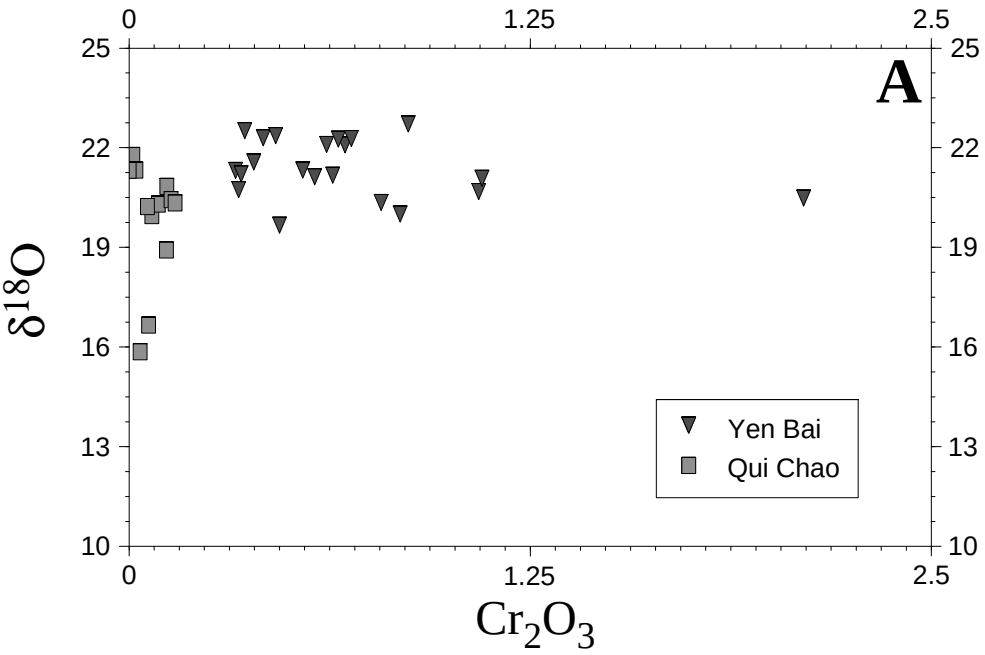
The fractionation of stable isotopes between minerals is temperature dependent and can be used as geothermometer. Mineral pairs of sample VC1, Cor-Cc, and V1, Sp-Fo, Chl-Fo, Chum-Fo, and Am-Fo, have been used to compare observed with calculated isotope fractionation. Analysed versus calculated isotope fractionation of silicate minerals of sample V1 differ significantly and are not in equilibrium. The isotope fractionation between Cor and Cc in sample VC1 is also completely in disequilibrium. The observed and calculated value differ by more than 8 permil delta ^{18}O. This

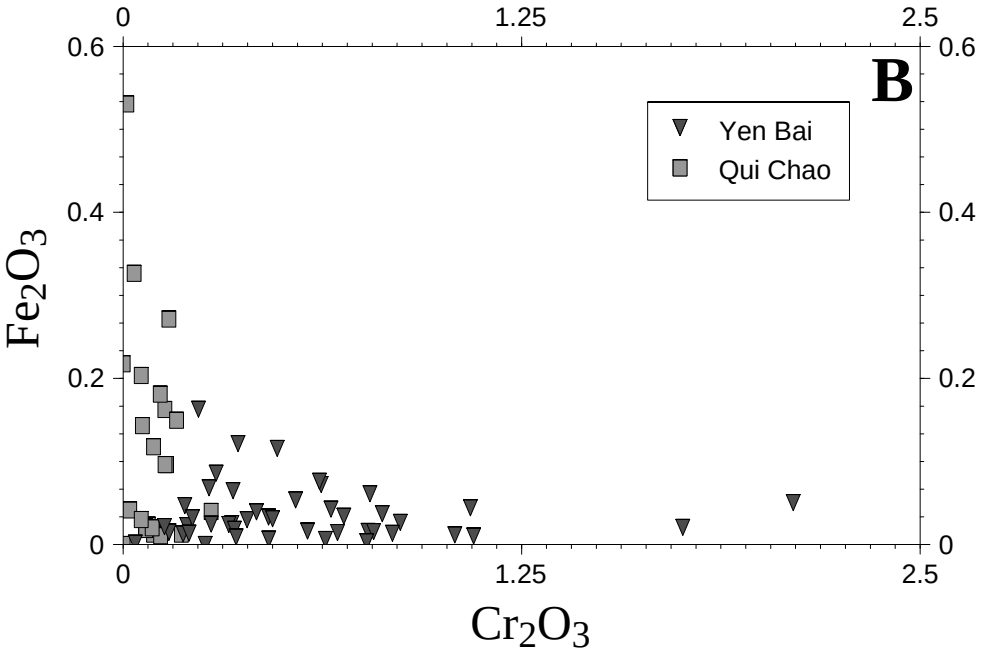
disequilibrium probably indicates a complicated formation history of these rocks. Detailed field work and more samples are needed for further investigations.

Chemical comparison of the ruby deposits of Yen Bai and Quy Chau, Vietnam

Chemical and oxygen isotope compositions of some rubies from the Yen Bai and Quy Chau mine have been determined (Figures 3A-C). These preliminary results should demonstrate that it is possible to use geochemical parameters to distinguish rubies from different areas. As shown in Figures 3A-C, rubies from both deposits can be distinguished by their oxygen isotope and trace element chemistry. More geochemical data of rubies is needed to demonstrate the diversity of occurring compositions. Further, the colour of corundum, mineral and fluid inclusions have to be documented and compared to the geochemical data. In a next step, rubies from nearby primary deposits have to be analysed and compared to rubies from the secondary deposits. By doing this we are able to relate rubies from the secondory deposits to their source. The oxygen isotope values from Yen Bai rubies are relatively homogeneous and show high values (delta ^{18}O of corundum = 20 - 22, Fig. 3A) which are comparable to those of the marble hosted rubies from Luc Yen (delta ^{18}O of corundum = 22.42 in sample VC1). The oxygen isotope values of rubies/sapphires from the Quy Chau area are not as homogeneous as from Yen Bai (Fig. 3A). Probably, several primary deposits have contributed to the secondary deposit in Quy Chau. The variability in colour of the extracted rubies and sapphires (colourless, blue, pink, red, and black) from this mine also supports this assumption.

The preliminary work demonstrates for the first time that Vietnamese rubies from the two alluvial deposits Quy Chau and Yen Bai are derived from primary marble hosted corundum deposits. Further, we could show that it is possible to distinguish rubies from both localities by their chemical and isotopic composition. However, more samples (from the primary deposit in Luc Yen and from the alluvial deposits Yen Bai and Quy Chau), more trace element analyses (LAB-ICP--MS), as well as fluid and mineral inclusions have to be investigated.





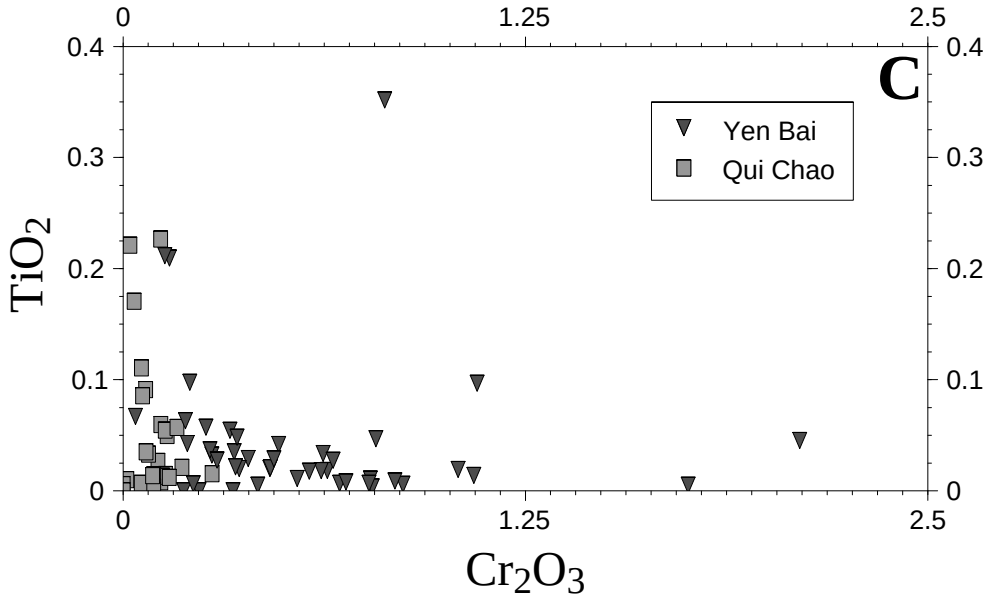


Figure 3: A) Cr_2O_3 - d ^{18}O plot of rubies from Quy Chau and Yen Bai. Oxygen stable isotope values are high, typical for sedimentary origin. Yen Bai rubies are more homogeneous in composition and may be of the same origin as the nearby rubies from marbles from Luc Yen. B) Cr_2O_3 - Fe_2O_3 values of of rubies from Quy Chau and Yen Bai. Rubies from Quy Chau and Yen Bai differ significantly in Cr_2O_3 values. C) Cr_2O_3 - TiO_2 values of of rubies from Quy Chau and Yen Bai.

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