

Temporal Emplacement Sequence of the South Nam Xe Carbonatites (Northwest Vietnam)

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Abstract: South Nam Xe carbonatites are located in northwest Vietnam and include calcio- and ferro-carbonatite dikes. This investigation on their petrography, mineralogy and whole rock chemistry aims to constrain temporal emplacement sequence of the carbonatites during their evolution. The calciocarbonatites are supposed to be formed in the first or second stage due to massive coarse-grained texture with an assemblage of calcite, typical magmatic alkaline silicates (aegirine, arfvedsonite), biotite, fluorapatite and magnetite. Their calcites show a high CaO/(MgO + Fe₂O₃ + MnO) ratio and a predominance of SrO over MnO (SrO = 3.81-3.98 wt.%; MnO = 0.66-0.78 wt.%). Rare earth elements (REE) tend to participate in rock-forming minerals rather than in isolated REE minerals. The ferrocarnatites are composed of magmatic and hydrothermal varieties and assumed to be formed in the third and/or fourth stage. Major minerals of the former include zoned ankerite, Sr-rich calcite, subhedral feldspar crystals, phlogopite and magnetite; fluorapatite, monazite and REE carbonates are minor resulting in a moderate REE concentration of 43,200 ppm. Meanwhile, the latter is predominant by syntax-texture REE fluorcarbonates and (Ba,Sr) sulphates. Further, the highest REE concentration (163,900 ppm) of the rock coupled with abundance of volatile minerals (fluorite, fluorcarbonates, sulphides) and ¹⁸O enrichment in the calcites ($\delta^{18}\text{O}_{\text{V-SMOW}} = 12.01\text{-}13.26\text{‰}$) is probably attributed to hydrothermal subjection in the last stage.

Key words: Carbonatite, South Nam Xe, emplacement sequence.

1. Introduction

Emplacement history and nature of igneous rocks have solid relations with mineral association, geochemical behavior of elements and phases, and are reflected by isotopic compositions. Carbonatite development petrologically and mineralogically is divided into four stages [1]. Of which, the first stage is usually calcitic and composed of magnetite, apatite, olivine, phlogopite/biotite, amphibole, or pyroxene. The second stage consists of calcite and/or dolomite, commonly together with pyrochlore, phlogopite/biotite, clinohumite, pyrrhotite and richteritic amphibole. These stages often contain xenoliths of fenitized wall rock. Third and four stages consist of dikes or dilatant/thin veins rich in ankerite with or without calcite, barite, chlorite, fluorite, hematite, pyrite,

quartz, rutile and strontianite.

2. Geological Setting

The South Nam Xe carbonatites are located in the northeastern part of the Song Da intracontinental rift structure in northwest Vietnam [2-7]. The zone extends from the Vietnam-China border to Ninh Binh coastal area (Vietnam), over a region about 430 km long and 40-80 km wide (Fig. 1), and is bounded by the Song Ma suture to the southwest, the Ha Noi basin to the southeast, and by the Fansipan, Tu Le, and Ailao Shan-Red River Shear Zone to the west [8]. The basement of the rift is heterogeneous, including Precambrian metamorphic rocks distributed along the southeastern margin of the Fansipan zone, and Lower to Middle Paleozoic formations and Carboniferous to Middle Permian shelf limestones, which are widely distributed in the Song Da basin and the northern Thanh Hoa area.

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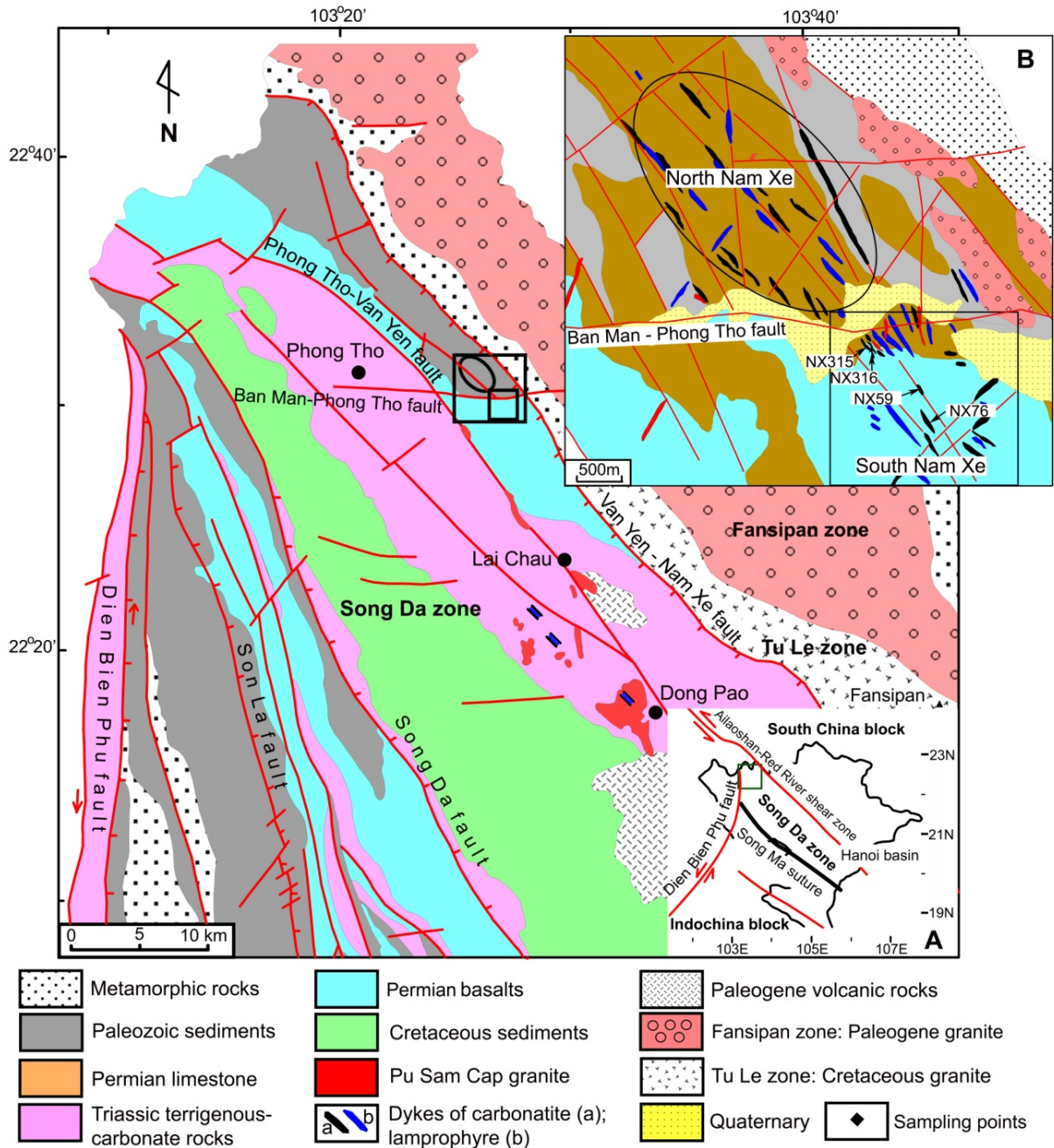


Fig. 1 Geological map of the Song Da structure zone (revised after My et al., 2005 [7]). Inset: A—sketch map showing location of the Song Da zone in northwest Vietnam; B—geological map of Nam Xe area, northwest Vietnam (modified after Chi et al., 2008 [15]).

In the Middle to Late Permian, magmatism erupted on the southwestern Yangtze Craton, producing a large igneous province known as the Emeishan flood basalts [9-11]. In the Late Permian to Triassic, tectonism resulted in graben formation in the Song Da zone, characterized by the eruption of Permian basalts

and trachytes. Later, the graben was filled with intercalated terrigenous and carbonate rocks during the Triassic. During the Late Triassic to Early Jurassic, the Song Da structure closed, due to uplift of the Indochina block, as represented by Late Triassic carbonate- and coal-bearing sediments [12, 13].

Highly potassic sub-volcanic intrusions and mafic dykes of Paleogene age are common, with occurrences restricted to northwest-southeast trending faults.

The South Nam Xe carbonatites including calciocarbonatites and ferrocarnatites are exposed as dykes or lenses up to several tens of meters wide and tens to hundreds of meters long (Fig. 1) [14, 15], which intruded Permian limestone and Permian basalts. The dykes are located at the intersection of the Ban Man-Phong Tho Fault and the axis of a syncline developed in Permian sediments [16]. On the basis of field and age evidence, Thanh et al. [14] and Chi et al. [15] concluded that the carbonatites originated from the same parental magma with the silicate rocks. However, trace element compositions as well as Sr-, Nd- and Pb isotopic data of these rocks do not show any apparent linkage [17].

C-O-Sr-Nd-Pb isotopic compositions and trace element data reveal that the carbonatites originated from a source contaminated by crustal materials mixing with enriched mantle sources prior to emplacement. Elevated $\delta^{18}\text{O}$ values of the ferrocarnatites accompanying with abundance of volatile-rich mineral

assemblages (e.g. fluorite, rare-earth-bearing fluorcarbonates, hydrous-thorite) and sulfur minerals are attributed to hydrothermal subjection at low temperatures [17].

3. Samples and Analytical Methods

3.1 Samples

The four carbonatite samples were collected for analysing petrography and geochemistry, which are as follows: (1) NX315 (Fig. 2a) is coarse-grained with a granular massive texture and contains calcite, aegirine, biotite, magnesio-arfvedsonite, and accessory magnetite, apatite, and pyrite; (2) NX316 (Fig. 2b) is foliated, fine- to medium-grained, and contains calcite, oriented phlogopite, fibrous amphibole, and minor magnetite and pyrite; (3) NX59 (Fig. 2c) is gray and contains ankerite, calcite, coarse-grained feldspar, apatite, (Ba,Sr) sulfates, and minor amounts of rare earth fluorcarbonates, monazite and thorite; and (4) NX76 (Fig. 2d) is pinkish due to the presence of rare earth fluorcarbonates and ankerite, and it also contains subordinate (Ba,Sr) sulfates and calcite, and minor monazite, fluorapatite, thorite, and sulfides (pyrite, sphalerite, galena).

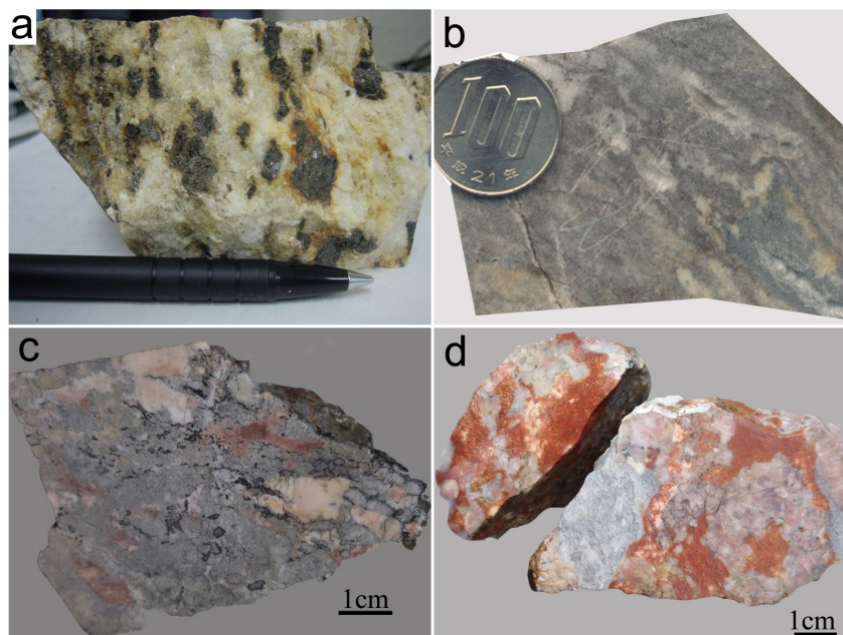


Fig. 2 Hand-samples of the South Nam Xe carbonatites: (a) coarse-grained calciocarbonatite (NX315); (b) foliated calciocarbonatite (NX316); (c, d) ferrocarnatites: c—NX59, d—NX76.

3.2 Analytical Methods

Four hand specimens were selectively cut and polished to make thin sections. All of them were observed under microscopes Olympus BX50 and Nikon LV 100 POL at Shizuoka University for an investigation of petrography and mineral chemistry.

Major-element chemical compositions of minerals were analyzed using a JEOLJXA 733 Electron Probe Micro Analyzer at Shizuoka University. Trace-element chemical compositions of minerals were determined using a JEOL Scanning Electron Microscope JSM-6610 situated at the National Science Museum of Japan. Details of analysing conditions, standard samples have been previously reported in Refs. [17, 18].

X-ray fluorescence (XRF) analysis was carried out by glass bead method [19, 20]. The rock powder was fused into a glass bead by a Phillips THG-5 bead sampler situated at Shizuoka University. Loss on ignition (LOI) was determined from total weight loss after ignition at 900-950 °C for 2 hours using a Yamato FO510 muffle furnace. Calibration was corrected by using standard samples' data from Geological survey of Japan [20].

Carbon-oxygen (C-O) isotopic measurement was conducted on CO₂ gas produced from reaction between calcite powder of the samples and phosphoric acid at 60 °C by using a Finnigan MAT-250 mass spectrometer (at Shizuoka University, Japan) [21]. Stable isotope values are expressed in the δ notation with $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1,000$, where R_{sample} and R_{standard} are the ¹³C/¹²C or ¹⁸O/¹⁶O ratios in the sample and international standard (V-PDB for $\delta^{13}\text{C}$, PDB—Pee Dee Belemnite; V-SMOW for $\delta^{18}\text{O}$, SMOW—Standard Mean Ocean Water), respectively.

4. Results

4.1 Petrography and Mineral Chemistry

Three types of carbonatites in South Nam Xe have been recognized based on the major-element

chemistry (see Section 4.2), petrography and mineral chemistry are as follows.

(1) Coarse-grained calciocarbonatite (Figs. 3a-3c) is primarily composed of calcite, biotite, aegirine-augite, magnesio-arfvedsonite, fluorapatite and magnetite. Calcite mostly forms large grains with sizes of 0.3-5.0 mm, although some calcite grains occur as inclusions in aegirine and biotite. Most of aegirine and biotite are coarse euhedral crystals up to a few centimeters in size and they are partly replaced by magnesio-arfvedsonite. Biotite also occurs as a replacement product at the rims of aegirine and within clusters of elongated apatite crystals. Magnesio-arfvedsonite has a euhedral, prismatic shape or occurs as rods within aegirine and biotite. Both magnesio-arfvedsonite and biotite have relatively high F contents (2.84 wt.% and 2.42 wt.%, respectively). Magnesio-arfvedsonite and aegirine have low Ti (TiO₂ = 0.19-0.41 wt.%) and Al (Al₂O₃ = 0.37-0.63 wt.%) contents. Fluorapatite occurs in two distinct morphologies: larger crystals form clusters of radiating euhedral prisms with a size of 0.8-2.3 mm, whereas smaller crystals occur as aggregates. Anhedronal pyrite occurs along cleavage faces or fractures within biotite. Secondary quartz is present in very small sizes (tens of microns) and extremely low abundance.

(2) Foliated calciocarbonatite (Figs. 3d-3f) comprises calcite, phlogopite, and magnesio-arfvedsonite, and is characterized by the absence of aegirine. Most of the calcite grains are subhedral to anhedral and are fine-to medium-grained (< 0.5 mm). Calcite is associated with small tabular grains of phlogopite that form bands resulting in the foliated texture of the rock. Compared with the coarse-grained calciocarbonatite, magnesio-arfvedsonite in the foliated calciocarbonatite has higher Mg contents (MgO = 17.23 wt.%), but is poorer in Fe (FeO = 11.03 wt.%); Ca and K contents in the phlogopite are also higher (CaO = 0.10 wt.%; K₂O = 10.04 wt.%).

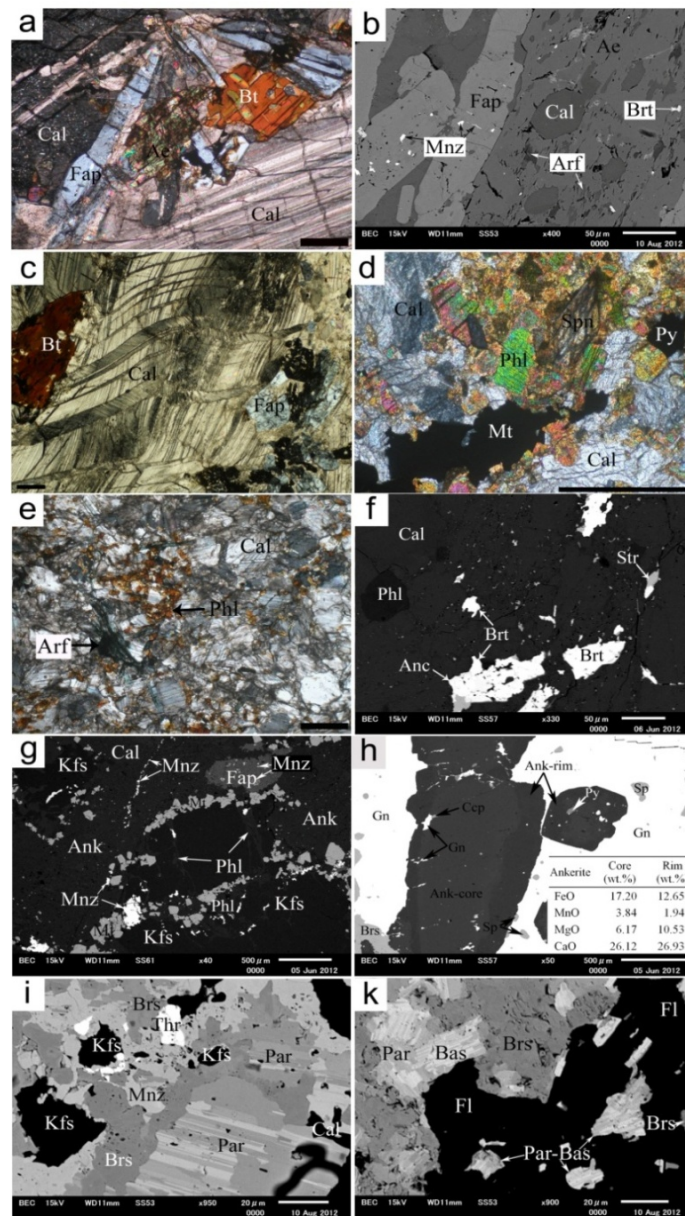


Fig. 3 (a-c) Photomicrographs showing mineral compositions of the South Nam Xe coarse-grained carbonatites, (c-f) foliated calciocarbonatites and (g-k) ferrocarnatites. (a) Fan-shaped elongated clusters of fluorapatite associated with coarse calcite, aegirine and biotite. (b) Fibrous arfvedsonite, calcite and barite within aegirine, monazite grains inside fluorapatite. (c) Calcites with curved cleavage. (d) Presence of sphene in an association with calcite, phlogopite, magnetite and pyrite. (e) Mineral association of calcite-arfvedsonite-phlogopite. (f) Micro-grained strontianite associated with barite, celestine and monazite along fractures of silicate minerals and/or calcite. (g) Association of ankerite, phlogopite, K-feldspar, calcite and fluorapatite: three modes of monazite: substitutes for apatite, isolated crystals and filling fractures, ankerite and feldspar surrounded by magnetite and phlogopite. (h) Zoned ankerite in the South Nam Xe ferrocarnatite containing sulphide minerals along cracks or cleavage planes. Chemical components of core and rim of the ankerite are present. (i) Lath-shaped Ca-rich parsite interlocking with normal parsite. (k) Association of fluorite, rare earth fluorocarbonates and (Ba,Sr) sulphates.

Scale bars in (a, c, d, e): 0.5 mm.

Mineral symbols: Cal—calcite, Ae—aegirine, Arf—arfvedsonite, Bt—biotite, Phl—phlogopite, Spn—Sphene, Fap—fluorapatite, Mt—magnetite, Py—pyrite, Spn—sphene, Str—strontianite, Ank—ankerite, Par—parsite, Bas—bastnäsite, Brt—barite, Brs—(Ba,Sr) sulphates, Mnz—monazite, Acy—ancylite, Kfs—potassium feldspar, Thr—thorite, Ga—galena, Ccp—chalcopyrite, Sp—sphalerite.

(3) Ferrocarbonatite (Figs. 3g-3k) has a more complex mineral assemblage relative to the calciocarbonatite.

Ankerite, calcite, rare earth carbonates, feldspar, fluorapatite, iron oxides, and Ba- and Sr-sulfates are common. MgO and FeO contents of the ankerite are 8.49 wt.% and 16.45 wt.%, respectively. Fluorite typically occurs as violet veins, or as small grains associated with rare earth carbonates and (Ba,Sr) sulfates. Pyrite, sphalerite, and galena occur as small crystals within all other mineral phases [16], or may form aggregates up to a few centimeters in size. Fluorine contents of the apatite from the ferrocarbonatites ($F = 3.70\text{-}3.94$ wt.%), are higher than apatite from the calciocarbonatites ($F = 3.50\text{-}3.58$ wt.%). These values are similar to those of fluorapatite from Bayan Obo carbonatites [22].

Trace-element and rare earth elements (REE)-enriched minerals in the carbonatites include synchysite-Ce, parisite-Ce, monazite-Ce, bastnäsitite-Ce, lanthanite, strontianite, uranpyrochlore, xenotime, cordylite-Ce, ancylite-Ce, barite, celestine, uraninite, and thorite [14, 15]. In the calciocarbonatites, these minerals occur rarely in the form of small grains with sizes of tens of microns (Figs. 3b and 3f), whilst they form relatively large grains and are common in the ferrocarbonatites (Figs. 3g, 3i and 3k). The most distinctive feature between the calciocarbonatites and ferrocarbonatites is the presence of barite and celestine, and near absence of intermediate compositions of

(Ba,Sr) sulfates in the calciocarbonatites, whereas in the ferrocarbonatite, they are dominant and associated with rare earth fluorcarbonates, fluorite and/or ankerite (Figs. 3i and 3k).

4.2 Whole Rock Major-Element Chemistry

As expected from the mineralogy, major-element data for the carbonatites exhibit a large range in CaO (15.07-55.57 wt.%) and Fe_2O_3 (2.19-9.67 wt.%) (Table 1), which allow classification of the Nam Xe carbonatites into calciocarbonatite and ferrocarbonatite [23]. The calciocarbonatites show high $\text{CaO}/(\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3 + \text{MnO})$ ratios (0.90-0.95) and the ferrocarbonatites have low $\text{CaO}/(\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3 + \text{MnO})$ ratios of 0.64-0.69 paired with low $\text{MgO}/(\text{Fe}_2\text{O}_3 + \text{MnO})$ ratios of 0.43-0.63. The carbonatites from South Nam Xe have low SiO_2 contents (< 12.18 wt.%) and negligible amounts of TiO_2 (< 0.13 wt.%). The high P_2O_5 content (6.22 wt.%) of the sample NX59 is due to its high modal abundance of apatite and monazite.

4.3 Trace-Element Chemistry

The South Nam Xe carbonatites have very high REE concentrations (REE from 3,400 to 6,100 ppm in calciocarbonatites and from 43,200 to 163,900 ppm in ferrocarbonatites) (Table 2). These REE concentrations are clearly higher than the average REE concentrations of worldwide carbonatites ([23], i.e. calciocarbonatite: 3,700 ppm; ferrocarbonatite: 10,400 ppm). The

Table 1 Major whole rock chemistry of the South Nam Xe carbonatites.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total
Standard												
JB-2	54.11	1.20	14.89	14.32	0.22	4.77	10.12	1.90	0.35	0.10	-	102.0
JG-2	78.66	0.06	13.24	1.03	0.01	0.19	0.79	3.48	4.24	0.02	-	101.7
Calciocarbonatite												
NX315	6.54	0.03	nd	2.30	0.27	0.65	55.75	0.11	0.09	1.11	29.32	96.2
NX316	10.58	0.13	0.81	2.19	0.40	2.91	52.04	0.16	1.12	0.02	27.61	98.0
Ferrocarbonatite												
NX59	12.18	0.03	1.72	9.67	1.34	4.72	28.12	0.09	1.58	6.22	23.44	92.3
NX76	8.99	0.04	0.86	3.71	0.52	2.68	15.07	0.10	0.75	0.40	28.23	61.4

nd: not detected.

Table 2 Trace element compositions (ppm) of the South Nam Xe carbonatites.

Element	JB-3	NX315	NX316	NX59	NX76
Ti	8,400	110	860	210	28.8
Rb	13.7	5.50	92.6	39.9	20.2
Sr	390	39,900	30,800	26,600	58,400
Y	23.9	150	140	340	460
Zr	88.1	46.0	1.42	1.48	1.66
Nb	2.16	2.33	63.3	24.1	3.75
Ba	226	11,100	6,700	30,000	82,500
La	8.18	1,600	840	11,400	50,300
Ce	20.8	2,900	1,600	20,400	79,300
Pr	3.19	290	160	2,200	7,600
Nd	15.4	980	590	7,400	23,300
Sm	4.16	130	82.9	960	2,100
Eu	1.22	32.8	21.1	210	400
Gd	4.62	76.2	56.7	440	670
Tb	0.67	8.09	5.65	37.6	49.1
Dy	4.58	36.0	34.5	130	160
Ho	0.89	5.95	5.56	14.7	17.9
Er	2.58	12.4	13.8	23.7	25.5
Tm	0.37	1.47	1.60	2.24	1.75
Yb	2.39	9.03	9.83	12.9	11.2
Lu	0.36	1.21	1.25	1.40	1.05
Hf	2.62	0.92	0.15	0.50	0.74
Ta	0.12	0.51	4.88	0.55	0.22
W	1.38	102	77.4	14.0	25.8
Pb	4.75	61.6	63.1	21.4	29.3
Th	1.27	5.03	1.70	1,100	2,200
U	0.45	1.15	55.2	310	94.0
ΣREE	69.4	6,100	3,400	43,200	163,900

carbonatites are LREE (light REE) enriched and have high La/Yb ratios (calciocarbonatites: 85-180; ferrocarbonatites: 890-4,500). The analyzed calciocarbonatites also show similar light- and middle-REE (La-Ho) concentrations to calciocarbonatite worldwide [23], the ferrocarbonatites are highly enriched in light- and middle-REE relative to ferrocarbonatite worldwide [23].

Concentrations of Sr (30,800-39,800 ppm in calciocarbonatites and 26,600-58,400 ppm in ferrocarbonatites) and Ba (6,700-11,100 ppm in calciocarbonatites and 30,000-82,500 ppm in ferrocarbonatites) are also distinctly higher than carbonatites worldwide (e.g. Refs. [23-25]). The LREE enrichment in these carbonatites is correlated with Sr and Ba enrichments and elevated La/Yb ratios.

The ferrocarbonatites are also characterized by very high Th (1,110-2,150 ppm) and U (94-306 ppm) concentrations. HFSE (i.e. Nb, Ta, Zr, Hf, and Ti) concentrations in the carbonatites are not as enriched in comparison to Ba, Sr, and REE.

4.4 Carbon-Oxygen Isotope Systematics

The South Nam Xe carbonatites are characterized by increasingly heavy oxygen isotopes at relatively constant $\delta^{13}\text{C}$ values. $\delta^{13}\text{C}$ values vary over a limited range ($\delta^{13}\text{C}_{\text{V-PDB}} = -2.74\text{‰}$ to -4.12‰), whereas $\delta^{18}\text{O}_{\text{V-SMOW}}$ values exhibit greater variability and define two groups. The lower $\delta^{18}\text{O}$ group (9.09-11.04‰) comprises the calciocarbonatites, whereas the higher $\delta^{18}\text{O}$ group (12.01-13.26‰) comprises the ferrocarbonatites. C-O isotope ratios of

the South Nam Xe carbonatites plot outside the primary magmatic carbonatite field proposed by Taylor et al. [26] ($\delta^{13}\text{C}_{\text{V-PDB}} = -4.0\text{‰}$ to -8.0‰ ; $\delta^{18}\text{O}_{\text{V-SMOW}} = 6.0\text{‰}$ to 10.0‰). Models of C-O isotopic fractionation developed by Comin Chiamonti et al. [27] show that the isotopic compositions of the calciocarbonatites appear in the higher right field of the magmatic evolution, whereas those of the ferrocarnatite are in the field of fluid-related hydrothermal recrystallization.

5. Discussion

5.1 Coarse-Grained Calciocarbonatite

Pyrite, a well-known product of hydrothermal or post-magmatic process, is present in all stages of the South Nam Xe carbonatites. However, the mineral assemblage of Sr-rich calcite associated with typical magmatic alkaline silicates (aegirine, biotite, arfvedsonite) and magnetite (Figs. 3a and 3b) observed in the coarse-grained calciocarbonatites must be formed in the first or second stage. Massive coarse-grained texture coupled with high $\text{CaO}/(\text{MgO} + \text{Fe}_2\text{O}_3 + \text{MnO})$ ratios (> 0.94) may be referred to as a sövite [23]. A study of spheroidal calcite inclusions in apatite shows that the early magmatic calcite contains a higher SrO content than MnO counterpart, and this value does not change considerably when the calcite interacts with late-stage fluids [28]. SrO and MnO variation in calcite from the calciocarbonatites resembles that of the early magmatic calcite since its SrO is predominant relative to MnO (SrO = 3.81-3.98 wt.%; MnO = 0.66-0.78 wt.%). Such types of calcite are also similar to those commonly found in early sövites [29] or in primitive carbonatite [30].

5.2 Foliated Calciocarbonatite

In the field, a narrow shear zone attached to fibrous actinolite and arfvedsonite was found between the two calciocarbonatites. The presence of sphene (Fig. 3d), a common mineral in calcium-rich metamorphic rocks, paired with a few kinked biotite and bended calcite in

the calciocarbonatite (Fig. 3c) assures an evidence of metamorphism and/or deformation occurred during and/or after coarse-grained calciocarbonatite emplacement. This hypothesis is supported by the oriented texture of the foliated calciocarbonatite. The higher Ca-, Mg-, and K-contents in fibrous arfvedsonite (Fig. 3e) of the foliated calciocarbonatite (CaO = 2.45 wt.%, MgO = 17.19 wt.%, K₂O = 3.39 wt.%) compared with those of the coarse-grained one (CaO = 1.73 wt.%, MgO = 13.35 wt.%, K₂O = 2.87 wt.%) might be attributed to calcium diffusion from calcite to silicates during metamorphism. Stability of major mineral assemblages (calcite, arfvedsonite, biotite/phlogopite, pyrite and magnetite) (Figs. 3e and 3f) is also consistent with a conclusion stated by Barker [1] that carbonatites emplaced before or during dynamic metamorphism preserve original distinctive magmatic mineral assemblages, trace element concentrations and ductility of calcite. Trace-element minerals such as ancylite, barite and strontianite are also maintained in the rock (Fig. 3f). However, rare-earth concentrations are somewhat lower than the coarse-grained variety (coarse-grained calciocarbonatite: 6,100 ppm; foliated calciocarbonatite: 3,400 ppm). The presence of monazite, barite, strontianite, celestine and REE carbonatites in the calciocarbonatites, even with tiny amounts, indicates the beginning of REE mineralization.

5.3 Ferrocarnatite

The South Nam Xe ferrocarnatite has a complex mineral association and mineral relationship, suggesting a complicated development. Although quartz (free silica) is mostly absent in ferrocarnatite as a late-stage product of carbonatitic sequential emplacement, feldspar is common (Fig. 3g). This is conformable with chemical behavior of silica in carbonatite proposed by Woolley and Kempe [23], which increases in the series from calcio- through magnesio- to ferrocarnatite, and probably as a result of desilicification of adjacent fenite. The

predominance of ankerite accompanying by rare-earth minerals, fluorite, barite, Ba-Sr sulfates and sulfides in variable proportions in the rock that can be named ankeritic carbonatites (Figs. 2c and 3g) is consistent with the third or fourth stage of the carbonatite evolution [1]. This mineral composition with nearly absence of quartz indicates weakly overprinted carbonatites when compared with those reported by Doroshkevich [31]. The presence of Sr-rich calcite in the composition is probably attributed to a weak re-equilibration and recrystallization of the calcite in presence of hydrothermal fluids. Deuteric feature of the ferrocarnatite is also documented by higher $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{V-SMOW}} = 12.01\text{-}13.26\%$) with constant $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{\text{V-PDB}} = -2.95$ to -4.12%) compared with the earlier calcite-rich carbonatites ($\delta^{18}\text{O}_{\text{V-SMOW}} = 9.40\text{-}11.04\%$) with constant $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{\text{V-PDB}} = -3.08$ to -3.93%) [1, 32].

There is a longstanding concern that ferrocarnatites may actually be products of hydrothermal rather than magmatic processes. However, evidence for magmatic origin of ferrocarnatites has been noted (e.g. Ref. [33]), whose ankerite is compositionally zoned and commonly associated with Sr-rich calcite, pure magnetite and pyrochlore. The assemblage of Sr-rich calcite together with zoned ankerite and subhedral coarse feldspar crystals surrounded by pure magnetite (Figs. 3g and 3h) resembles that reported by Thomson et al. [33] and probably is typical product of magmatism. The aggregation of stubby to hexagonal zoned apatite associated with monazite is also similar to that documented from magmatic carbonatites elsewhere (e.g. Taourirt carbonatite [29], Jacupiranga carbonatite [34]). Although the $\delta^{13}\text{C}$ values of the ferrocarnatites ($\delta^{13}\text{C}_{\text{V-PDB}} = -2.95$ to -4.12%) are higher than those of primary carbonatites [26], they are as same as those of the calciocarnatite ($\delta^{13}\text{C}_{\text{V-PDB}} = -2.74$ to -3.93%) suggesting a genetic link between them. The elevated values are attributed to contamination by crustal materials prior to

emplacement [17].

However, many known-ferrocarnatites are hydrothermal in origin or magmatism overprinted by hydrothermal events, particularly those accompanying with REE mineralization (e.g. Refs. [31, 35-38]). In addition to characteristics pointed to similarities to magmatic origin of the ferrocarnatite as mentioned previously, the widespread occurrence of REE fluorocarnates, fluorite, barite and other Ba-Sr sulfates, strontianite and sulfides (galena, sphalerite, pyrite and chalcopyrite) (Figs. 3h-3k) would be usually pertained to hydrothermal activities [31, 39]. Relationship among minerals and rock texture, as well as presence of F^- , SO_4^{2-} and S^- components in the fluids also supported to this assumption: (1) F-contents in the REE carbonates and apatite reach up 5.91 and 3.94 wt.%, respectively; (2) Most REE carbonates are partly dissolved by later SO_4^{2-} -bearing fluid, or infillings in solution cavities or voids among the rest minerals of the Ba-Sr sulfates (Figs. 3i and 3k), resulting in dissolved or flowing textures of the rock, respectively; (3) Syntaxy among synchysite, parisite and bastnaesite (Figs. 3i and 3k) should be formed in the final stage of carbonatite evolution; (4) Sulfide minerals fill gaps along zoned ankerite (Fig. 3h). These suggest an existence of exterior factors such as meteoric water at low temperatures and shallow levels.

The samples of igneous carbonatites have the lowest rare-earth abundances and show weakly fractionated patterns ($\Sigma\text{REE} = 6,100$ ppm and $\text{La/Lu} = 1,330$). Much higher REE concentrations of 43,000-163,900 ppm and La/Lu ratios of 8,170-48,130 are also typical features for late-stage of the ferrocarnatite compared with the calciocarnatite, and are attributed to influence of hydrothermal process. Trace elements additionally reveal difference in chemical behavior characteristics due to carbonatite evolution stage. Generally, in early stage, rare-earth elements tend to participate in rock-forming minerals in terms of cation substitution; meanwhile they incline

to separate into isolated minerals with an increase in quality and distribution in later stage. This phenomenon is easily observed in the South Nam Xe carbonatites.

The presence of a considerable volume of fluorite at South Nam Xe, coupled with the high F content of hydroxyl-bearing minerals (amphibole, biotite/phlogopite, apatite), suggests that the melts/fluids responsible for mineralization were initially extremely F-rich, which could have led to the dominance of fluor complexes due to a high F/Cl ratio in the fluid.

6. Conclusion

The South Nam Xe carbonatite has a complex geological history and comprises both magmatic stage and hydrothermal/post-magmatic alteration. There is no doubt that the emplacement of the calciocarbonatites preceded that of the ferrocyanatite. The coarse-grained variety represents a highly igneous magma, which is typical for Sr-rich calcite-apatite-magnetite-aegirine-biotite-arfvedsonite association. The foliated calciocyanatite has experienced metamorphism, but exhibits relatively similar mineral and trace element compositions to the coarse-grained counterpart. Coarse-grained texture of the ferrocyanatite and the mineral composition of ankerite, feldspar, magnetite, phlogopite, calcite and apatite, accompanying with high REE contents might belong to slow cooling late magmatic process which partly is influenced by hydrothermal events. Mineral assemblage of REE fluorocyanates, fluorite, barite and other sulfates, strontianite and sulfides, coupled with elevated $\delta^{18}\text{O}$ values and extremely high REE abundances suggests a final magmatic stage strongly subjected to hydrothermal activities of the ferrocyanatite.

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