

A mechanism for Na incorporation in garnet: An example from garnet in orthogneiss from the Su-Lu terrane, eastern China

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ABSTRACT

Sodian and yttrian (Na-Y) garnet occurs in orthogneisses of the Su-Lu terrane of eastern China with major quartz, microcline, and albite and subordinate biotite, titanite, hematite, and zircon. Acmite-rich pyroxene, muscovite, epidote, allanite, and hastingsitic amphibole occur in a few of the samples. The Na-Y garnet can be divided into almandine-spessartine-grossular [Al > 1.6 per formula unit (pfu) for O = 12, hereafter denoted as Al-garnet], and andradite-spessartine ($\text{Fe}^{3+} > 1.3$ pfu, hereafter denoted as Fe^{3+} -garnet) groups. Average composition of the Al-garnet in each sample ranges from $\text{Alm}_{35}\text{Sps}_{13}\text{Prp}_1\text{Grs}_{49}\text{Adr}_2$ to $\text{Alm}_{21}\text{Sps}_{67}\text{Prp}_0\text{Grs}_5\text{Adr}_7$. The Fe^{3+} -garnet contains a calderite component (Cdr) and its composition is $\text{Alm}_{4-7}\text{Sps}_{10-21}\text{Prp}_{1-2}\text{Adr}_{59-81}\text{Cdr}_{3-12}$. Na, Y, and Yb contents of the Al-rich garnet reach 0.37, 1.46, and 0.42 oxide wt%, respectively, and $\text{Na}/(\text{Y} + \text{Yb}) = 0.99 \pm 0.16$. The Fe^{3+} -garnet contains up to 0.11, 2.1, and 0.48 wt% of Na_2O , Y_2O_3 , and Yb_2O_3 , respectively, and its $\text{Na}/(\text{Y} + \text{Yb})$ value (0.17 ± 0.1) is lower than that of the Al-garnet. We conclude that Na, Y, and Yb are incorporated in the Al-rich garnet by the $^{[8]}\text{Na}^{[6]}(\text{Y}, \text{Yb})(\text{Ca}, \text{Mn})_{-2}$ substitution, whereas in the Fe^{3+} -garnet, Y and Yb are dominantly incorporated by the $^{[8]}(\text{Y}, \text{Yb})^{[4]}(\text{Al}, \text{Fe}^{3+})(\text{Ca}, \text{Mn})_{-1}\text{Si}_{-1}$ substitution with up to 3 mol% Y + Yb for Ca + Mn. Comparison of $\text{Na}/(\text{Y} + \text{Yb})$ of garnets in the orthogneisses and in some pegmatites implies that increasing pressure favors incorporation of Na with Y and Yb, and that under the albite-epidote amphibolite facies or higher-pressure conditions, Y and Yb probably substitute into the garnet structure by $^{[8]}\text{Na}^{[6]}(\text{Y}, \text{Yb})(\text{Ca}, \text{Mn})_{-2}$, instead of the $^{[8]}(\text{Y}, \text{Yb})^{[4]}(\text{Al}, \text{Fe}^{3+})(\text{Ca}, \text{Mn})_{-1}\text{Si}_{-1}$ -type substitution effective under lower-pressure conditions.

INTRODUCTION

Na incorporation in garnet has been described from both experimental and natural occurrences. Na substitutions in garnet such as $^{[8]}\text{Na}^{[6]}\text{TiCa}_{-1}\text{Al}_{-1}$, $^{[8]}\text{Na}^{[4]}\text{PCa}_{-1}\text{Si}_{-1}$, and $^{[8]}\text{Na}^{[6]}\text{SiCa}_{-1}\text{Al}_{-1}$ have been proposed based on high pressure experiments under several GPa (e.g., Ringwood and Lovering, 1970; Ringwood and Major, 1971; Thompson, 1975). Gasparik (1989) clearly showed the existence of a transition between pyroxene and garnet and the wide range of solid solution between $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{NaMg}_2\text{AlSi}_4\text{O}_{12}$ at 10.0–16.5 GPa and 1350–1650 °C.

Natural examples of Na-bearing garnets were mostly reported from mantle xenoliths (e.g., Sobolev and Lavrent'ev, 1971; Bishop et al., 1976; Reid et al., 1976; Moore et al., 1991) and ultra high-pressure metamorphic

rocks (Schertl et al., 1991), and thus Na in garnet has been considered to have potential use as an indicator of pressure (Meagher, 1982). However, concentrations of Na have also been reported in yttrian garnets from pegmatites (Imori, 1938; Vormea et al., 1966; Kasowski and Hogarth, 1968; Wakita et al., 1969). These data imply the possibility of a Na-Y coupled substitution in garnet under low pressure conditions (e.g., Jaffe, 1951), but they were all obtained by wet chemical analyses and included values for H_2O , CO_2 , and K_2O . Therefore, there is reason to suspect the presence of impurities in the analyzed garnets. The extent to which Na-bearing garnet can be stable under low-pressure conditions remains uncertain.

This paper reports an occurrence of sodian and yttrian garnets (here denoted as Na-Y garnet), with up to 0.37 wt% Na_2O , 2.1 wt% Y_2O_3 , and 0.48 wt% Yb_2O_3 , in orthogneisses from the Su-Lu terrane of eastern China, and

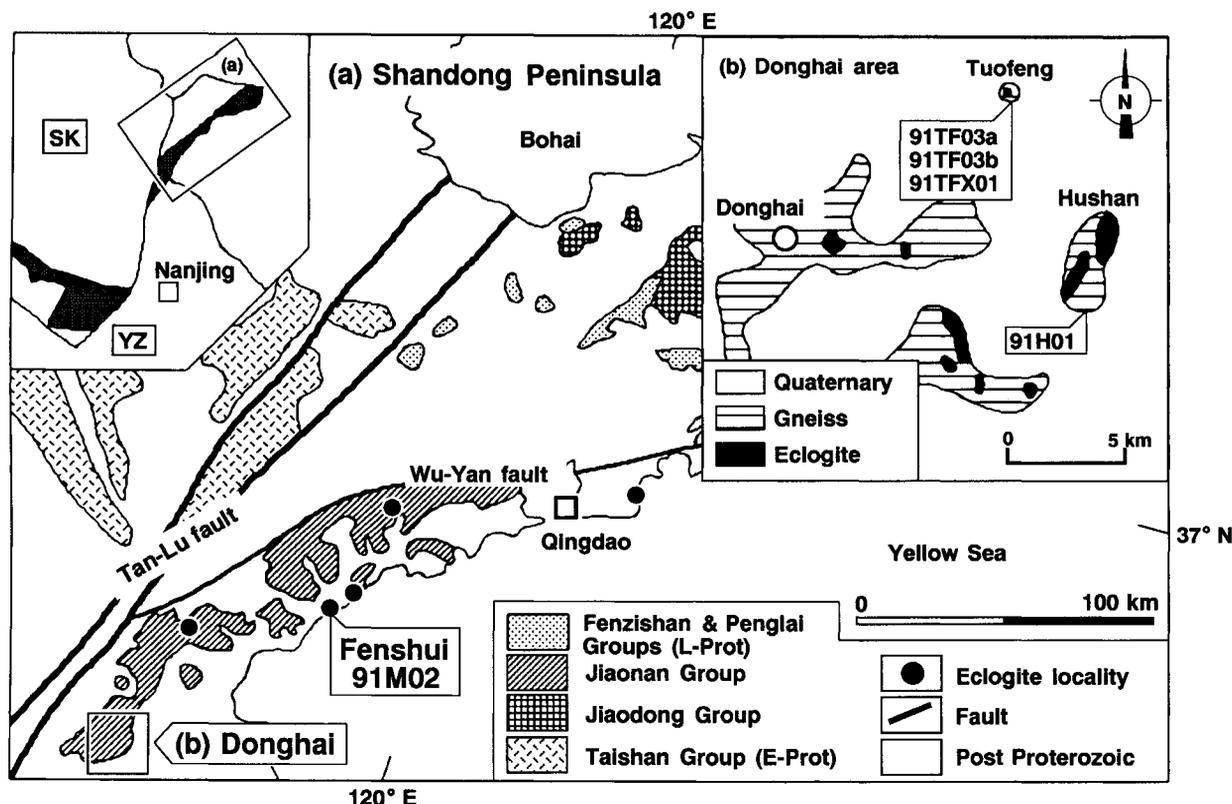


Fig. 1. Geologic sketch map of northern Jiangsu and southern Shandong Provinces, eastern China (simplified from the Bureau of Geology and Mineral Resources of Shandong Province, 1991) (a) with sample localities, including an enlargement of the Donghai region (b). Major constituent rock-types of the Taishan Group are migmatitic gneiss and granitoid, and those of the Jiaodong and Jiaonan Groups are ortho- and paragneisses, basic

granulite, and amphibolite. The Fenzishan and Penglai Groups are mainly composed of metasediments and unmetamorphosed siliceous and calcareous sediments, respectively. Abbreviations are: SK = Sino-Korean craton; YZ = Yangtze craton; Tan-Lu fault = Tancheng-Lujiang fault; Wu-Yan fault = Wulian-Qingdao-Yantai fault; L-Prot = late Proterozoic; E-Prot = early Proterozoic.

discusses the substitution relations of Na and Y + Yb into garnet. This example clearly documents the Na-Y coupled substitution in garnet.

REGIONAL GEOLOGY

The Na-Y garnet studied here was found in orthogneisses from Donghai, Jiangsu Province and Fenshui, Shandong Province of eastern China (Fig. 1). These provinces are cut by the Wulian-Qingdao-Yantai (Wu-Yan) fault (Yu, 1990). On the northern side of the fault are middle Proterozoic ortho- and paragneisses (1500–1720 Ma; Enami et al., 1993a). On the southern side of the Wu-Yan fault lies the Su-Lu ultra high-pressure terrane where coesite eclogite and garnet periodotite blocks occur sporadically in orthogneiss and amphibolite (reviewed by Okay and Sengör, 1992, and Zhang et al., 1993). The metamorphic conditions of eclogites are estimated at >2.6 GPa and 730–880 °C (e.g., Hirajima et al., 1992; Enami et al., 1993b). The sequence of eclogite and the surrounding country rocks was subjected to greenschist to albite-epidote amphibolite facies metamorphism of Mesozoic

age (Cong et al., 1992; Ishiwatari et al., 1992). In the country rocks there is no clear evidence for ultra high-pressure metamorphism prior to the greenschist to albite-epidote amphibolite facies stage. Preliminary results from the garnet + biotite geothermometer (e.g., Indares and Martignole, 1985; Dasgupta et al., 1991) gives metamorphic temperature of about 400–500 °C at $P = 0.5$ GPa for the orthogneisses. Coexisting feldspars in the orthogneisses have nearly pure end-member compositions ($Or > 91$ and $Ab > 96$) showing they equilibrated at temperatures below 450 °C (Fuhrman and Lindsley, 1988). The metamorphic pressure is estimated at 0.5 GPa at 450 °C based on the jadeite content of aegirine-augite and using the calibration of Banno (1986) (cf. Enami et al., 1993c). The Si content of muscovite coexisting with biotite, potassium feldspar, and quartz reaches 6.7 per formula unit (pfu) for $O = 22$ and gives $P = 0.7$ GPa at 450 °C (Massonne and Schreyer, 1987). The estimated P - T conditions are inconclusive but are consistent with the presence of the hastingsitic amphibole + albite + epidote assemblage in some orthogneisses (cf. Table 1).

MINERAL ASSEMBLAGE AND WHOLE ROCK CHEMISTRY

The orthogneisses in the Su-Lu terrane can be divided into two-mica and mica-poor types. The two-mica gneiss is composed mainly of quartz, microcline, albite, biotite, phengitic muscovite, epidote, hematite, titanite, and zircon. The mica-poor gneiss is similar in assemblage to the two-mica gneiss except that it contains only traces, if any, of muscovite. The absence of chlorite is attributed to the low $(Al - Na - K)/(Fe^{2+} + Mn + Mg)$ ratio in the bulk compositions of these orthogneisses (cf. Appendix Table 1). Acmite-rich pyroxene occurs in some mica-poor gneisses. Garnet occurs locally in anhedral crystals 20–700 μm in diameter and is distributed irregularly in a matrix of equigranular quartz and feldspars in both the two-mica and mica-poor gneisses. The Na-Y garnet was found only in the mica-poor gneiss. The garnet crystal includes fine-grained titanite, feldspars, and quartz and is considered to be metamorphic in origin.

A detailed mineralogical study was carried out on five mica-poor orthogneisses containing Na-Y garnet: 91TF03a, 91TF03b (see also Enami et al., 1993c), and 91TFX01 from Tuofeng in the Donghia area, 91H01 from Hushan in the Donghai area, and 91M02 from Majiagou in the Fenshui area (Fig. 1 and Table 1). The Tuofeng samples have alkalic bulk compositions $(Na + K)/Al = 0.99$ (Appendix Table 1) with aegirine ($Aug_{5-8}Jd_{7-8}Acm_{85-87}$) or aegirine-augite ($Aug_{53-58}Jd_{8-10}Acm_{34-37}$), abbreviations after Kretz (1983). The other two samples contain epidote and their $(Na + K)/Al$ value of 0.95 is slightly lower than that of the Tuofeng samples. The Na-Y orthogneisses are all depleted in MgO (<0.2 wt%) and CaO (<0.7 wt%). Y content is 45–110 ppm, in the range of ordinary granitic rocks (3–160 ppm; Herrmann, 1970). Rare earth element contents and their chondrite-normalized pattern are also similar to those of granitic rocks (Fig. 2). P_2O_5 content is <0.02 wt%. The low P_2O_5 content was probably insufficient for xenotime (YPO_4) to form, and thus Y and other heavy REE were available for preferred incorporation in garnet.

ANALYTICAL PROCEDURES

Major constituent minerals were analyzed with a JEOL electron-probe microanalyzer JXA-733 with three

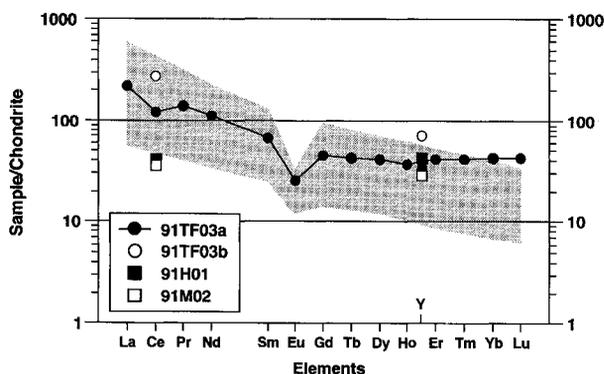


Fig. 2. The range of REE and Y contents in Na-Y garnet-bearing orthogneisses. Shaded part shows the range of REE content in granitic rocks compiled by Cullers and Graf (1984).

wavelength-dispersive spectrometers at Nagoya University. Accelerating voltage, specimen current, and beam diameter were kept at 15 kV, 12–20 nA on Faraday cup, and 3 μm , respectively. Well-characterized natural minerals and synthetic materials were used as standards, including Y, Yb, and Er metals. The ZAF method was employed for matrix correction. Spectrometer step scanning analyses for Na and other minor elements were made to inspect the peak profiles and to determine suitable spectrometer positions for background measurements. Although detection limits (2σ level) vary slightly depending on specimen current and counting times, they are as follows in most analyses: Na_2O 0.006–0.007 wt%, Y_2O_3 0.02–0.04 wt%, Yb_2O_3 0.020–0.032 wt%, TiO_2 0.010–0.015 wt%, ZnO 0.019–0.023 wt%, and P_2O_5 0.005–0.010 wt%.

Representative analyses of garnet are given in Table 2. Garnet is depleted in Al with a significant andradite component, and its Fe^{3+} content was estimated by assuming a total cation of 8 for 12 O atoms.

RESULTS AND DISCUSSION

Different samples of garnet show a significant compositional variation and can be divided into aluminian (Al > 1.6 pfu, hereafter denoted as Al-garnet) and ferrian (estimated $Fe^{3+} > 1.3$ pfu, hereafter denoted as Fe^{3+} -

TABLE 1. Mineral assemblages of Na-Y garnet-bearing orthogneisses from the Su-Lu terrane, eastern China

Sample	Grt	Qtz	Ab*	Mc*	Ms**	Bt	Ep†	Aln	Agt†	Hs	Ttn‡	Hem	Zrn
91TF03a	+	+	0	91	6.7	+		+	34		86	+	+
91TF03b	+	+	1	+		+		+	37		81	+	+
91TFX01	+	+	0	91					87		90	+	+
91H01	+	+	2	92		+	35	+§		+	80	+	+
91M02	+	+	1	93	6.7	+	28				75	+	+

Note: abbreviations are from Kretz (1983).

* Anorthite and orthoclase mole percent for Ab and Mc, respectively.

** Si per formula unit for O = 22, Ms in 91TF03a occurs only as inclusion in Ab.

† Pistacite and acmite mole percent for Ep and Agt, respectively.

‡ $Ti/(Ti + Al + Fe^{3+}) \times 100$.

§ Occurs only as core of Ep.

|| $Al_2O_3 = 11.7$ wt%.

TABLE 2. Representative analyses of Na-Y garnet in the Su-Lu orthogneisses and Y-rich pegmatite

	Orthogneiss						Pegmatite*	
	91TF03a			91TF03b	91TFX01	91H01	91M02	GSJ-M18062
	(Al-gar)	(Fe ³⁺ -gar)	(Fe ³⁺ -gar)	(Fe ³⁺ -gar)	(Al-gar)	(Al-gar)	(Al-gar)	(Al-gar)
Weight percent oxides								
SiO ₂	36.1	34.1	33.8	35.0	36.9	36.8	38.2	34.7
TiO ₂	0.26	0.44	0.33	0.45	0.14	0.18	0.10	0.00
Al ₂ O ₃	20.1	4.91	4.76	2.47	20.6	17.9	20.6	19.9
Y ₂ O ₃	1.19	1.49	2.10	0.89	0.76	1.02	0.33	3.15
Er ₂ O ₃	—	0.14	—	—	—	—	—	—
Yb ₂ O ₃	0.24	0.21	0.43	0.16	0.06	0.24	0.07	0.56
FeO**	14.6	22.6	22.2	25.1	11.1	20.7	13.3	15.8
MnO	21.7	14.1	13.3	6.18	28.0	9.85	6.21	24.5
MgO	0.03	0.26	0.24	0.04	0.03	0.11	0.14	0.00
ZnO	—	0.02	0.10	0.04	0.07	0.00	0.02	0.01
CaO	3.48	18.1	18.5	26.8	3.61	12.0	20.6	1.64
Na ₂ O	0.372	0.093	0.094	0.021	0.244	0.236	0.079	0.093
Total	98.1	96.5	95.9	97.2	101.5	99.0	99.6	100.4
Cations = 8								
Si	3.010	2.967	2.966	2.984	2.978	3.011	3.009	2.895
Ti	0.016	0.029	0.022	0.029	0.008	0.011	0.006	0.000
Al	1.975	0.504	0.492	0.248	1.959	1.726	1.912	1.956
Y	0.053	0.069	0.098	0.040	0.033	0.045	0.014	0.140
Er	—	0.004	—	—	—	—	—	—
Yb	0.006	0.006	0.012	0.004	0.002	0.006	0.002	0.014
Fe ³⁺ †	0.000	1.441	1.438	1.685	0.073	0.217	0.056	0.116
Fe ²⁺ †	1.018	0.203	0.190	0.104	0.676	1.199	0.821	0.986
Mn	1.533	1.039	0.988	0.446	1.914	0.682	0.414	1.731
Mg	0.004	0.034	0.032	0.005	0.003	0.013	0.017	0.000
Zn	—	0.001	0.006	0.003	0.004	0.000	0.001	0.001
Ca	0.311	1.688	1.739	2.448	0.312	1.052	1.738	0.146
Na	0.060	0.016	0.016	0.003	0.038	0.037	0.012	0.015

Note: abbreviations are: Al-gar = aluminian garnet; Fe³⁺-gar = ferrian garnet. K is below detection limits.

* Yttrian garnet in Y-rich pegmatite described by Iimori (1938) and Wakita et al. (1969).

** Total Fe as FeO.

† Calculated values (see text).

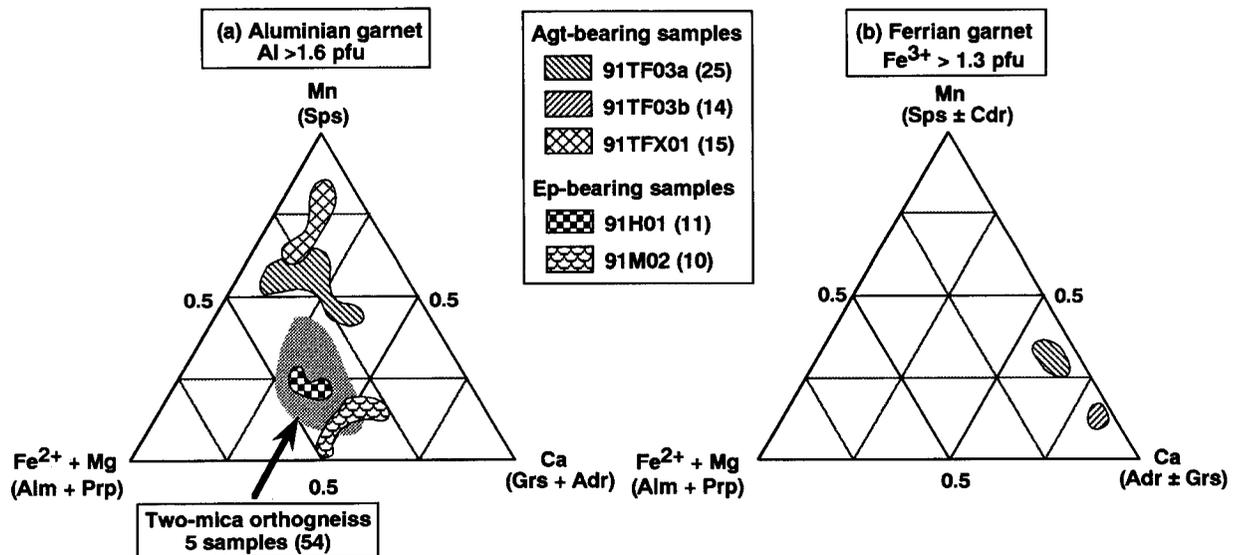


Fig. 3. Compositional ranges of (a) aluminian garnet and (b) ferrian garnet in the Mn-(Fe²⁺ + Mg)-Ca system. Numbers in parentheses are numbers of analytical data. Abbreviations are: Sps = spessartine; Alm = almandine; Prp = pyrope; Grs = grossular; Adr = andradite; Cdr = calderite; pfu = per formula unit for O = 12. Others are defined in Table 1.

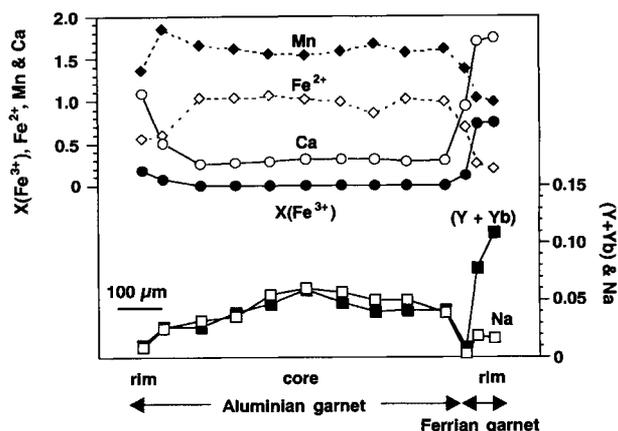


Fig. 4. Compositional profile of a zoned garnet in 91TF03a. $X_{Fe^{3+}} = Fe^{3+}/(Al + Fe^{3+})$.

garnet) groups (Fig. 3). The Fe^{3+} -garnet coexists with acmite-rich pyroxene. The Al-garnet is almandine-spessartine-grossular solid solution ($Alm_{35}Sps_{13}Prp_1Grs_{49}Adr_2$ - $Alm_{21}Sps_{67}Prp_0Grs_5Adr_7$), whereas the Fe^{3+} -garnet is andradite-spessartine-calderite solid solution ($Alm_{4-7}Sps_{10-21}Prp_{1-2}Adr_{59-81}Cdr_{3-12}$) (Fig. 3). The Al-garnet in epidote-bearing samples has a similar compositional range to that in two-mica orthogneisses. Coarse-grained garnet in 91TF03a is strongly zoned with an almandine-spessartine core, a slightly andraditic inner rim, and a calderitic outermost rim (Fig. 4; also Enami et al., 1993c). A Becke's line is observed at the boundaries between the three zones and corresponds to distinct compositional breaks.

Amounts of minor elements vary between the Al- and Fe^{3+} -garnets. The Na content in the Al-garnet varies from 0.09 ± 0.07 oxide wt% in 91M02 to 0.27 ± 0.05 oxide wt% in 91TFX01, and the Na content in the Fe^{3+} -garnet is <0.11 wt%. (Enami et al., 1993c, erroneously reported Na content of an Al-garnet in 91TF03a as 0.02 wt%. This content should be 0.20 wt%.) A positive correlation was observed between Y and Yb with $Yb/Y = 0.06-0.22$ (average value in each sample). The Yb/Y value is similar to that of yttrian garnets in pegmatites (0.10-0.29; Vorma et al., 1966; Wakita et al., 1969; this study, Table 2). A positive correlation between the Na and Y + Yb contents is observed in an Al-garnet core, in which these elements gradually decrease outward (Fig. 4). The Er_2O_3 content at a (Y + Yb)-rich spot of calderitic garnet in 91TF03a is 0.14 wt% (detection limit 0.04 wt% for 2σ level). The P_2O_5 content is <0.01 wt% in both the Al- and Fe^{3+} -garnets.

Na-Y coupled substitution

Na^+ substitution for Ca and Mn^{2+} in an eightfold-coordinate site could be charged balanced by one of the following substitutions: (1) a trivalent cation (e.g., Y^{3+}) in an eightfold-coordinate site, (2) a tetravalent cation (e.g., Si^{4+} ; Sobolev and Lavrent'ev, 1971; Ti^{4+} ; Bishop et al., 1976; Reid et al., 1976) in a sixfold-coordinate site,

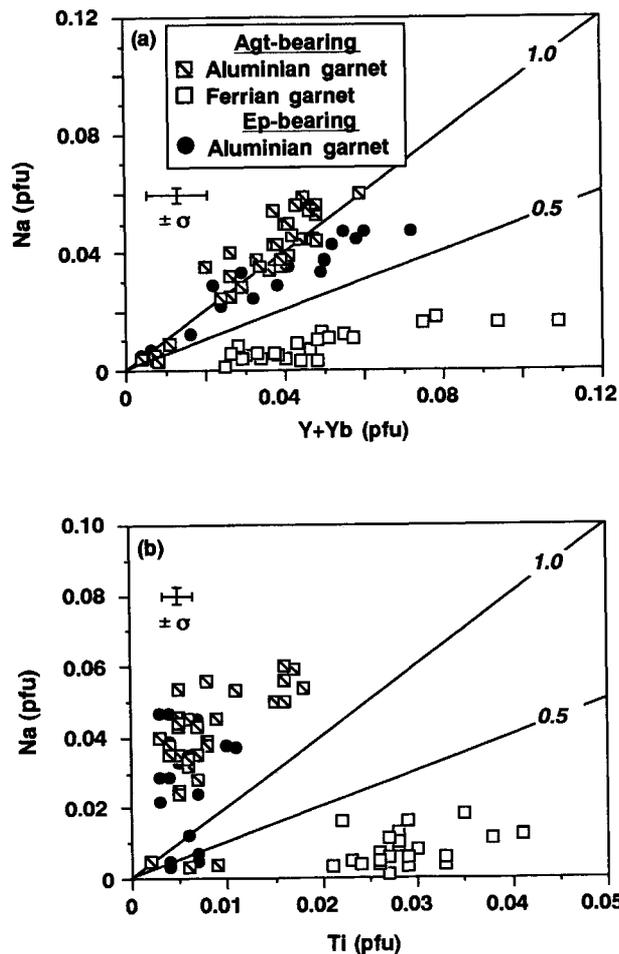


Fig. 5. Atomic correlations between Na and Y + Yb (a) and Na and Ti (b) of aluminian and ferrian garnets. Numbers in italics indicate $Na/(Y + Yb)$ in a and Na/Ti in b. Abbreviations are defined in Table 1 and Fig. 3.

(3) a pentavalent cation (e.g., P^{5+} ; Thompson, 1975) in a fourfold-coordinate site, or (4) a monovalent anion (F^- , etc.) for O^{2-} . However, the P content of Na-Y garnets is <0.001 pfu, and excess Si was not observed. Thus, large valence elements are not sufficient to account for the presence of Na by the Na-(Si,P,Ti) coupled substitutions in these garnets. Cl and F are below the detection limits for both garnet types in 91TF03a and 91TF03b (detection limits: 0.01 wt% for Cl and 0.05 wt% for F).

There is a strong positive correlation between Na and Y + Yb contents of Al-garnets (correlation coefficient = 0.90) and the $Na/(Y + Yb)$ value is close to unity: average value in each sample varies from 0.79 to 1.19 (Fig. 5a). Al-garnets in aegirine- or aegirine-augite-bearing samples tend to have slightly higher $Na/(Y + Yb)$ than those in epidote-bearing samples. On the other hand, the $Na/(Y + Yb)$ of Fe^{3+} -garnets is lower than that of Al-garnets and 0.17-0.18 in average (Fig. 5b). The Na-(Y + Yb) positive correlation with Al-garnet and the negative

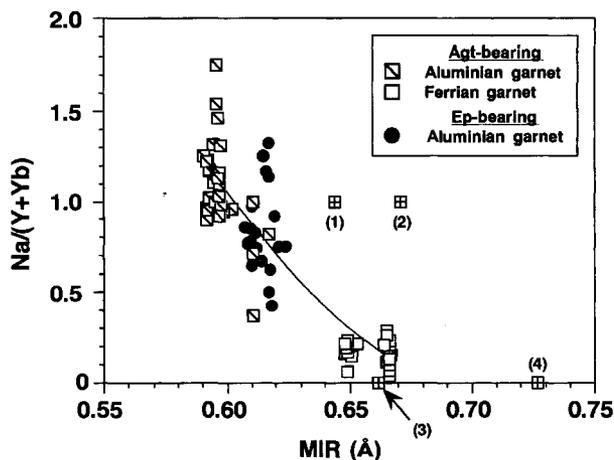


Fig. 6. Correlation between $\text{Na}/(\text{Y} + \text{Yb})$ and MIR (mean ionic radius) of the Na-Y garnets. $\text{MIR} = \sum (r_i^c \times N_i) / \sum N_i$, where N and r represent numbers of atoms and radius for the appropriate coordination, respectively, superscript c represents coordination numbers, and subscript i refers to name of atom. Numbered points (1), (2), (3), and (4) indicate Y-bearing end-members $\text{Na}_{1.5}\text{Y}_{1.5}\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Na}_{1.5}\text{Y}_{1.5}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$, $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$, and $\text{Y}_3\text{Fe}_2^{3+}\text{Fe}_3^{3+}\text{O}_{12}$, respectively. Abbreviations are defined in Table 1.

correlation between $\text{Na}/(\text{Y} + \text{Yb})$ and $X_{\text{Fe}^{3+}}$ [$= \text{Fe}^{3+}/(\text{Al} + \text{Fe}^{3+})$] are also documented in a zoned garnet (Fig. 4).

In the eightfold-coordinate site, effective ionic radii of Na^+ (1.18 Å), Y^{3+} (1.019 Å), and Yb^{3+} (0.985 Å) are similar to those of Ca^{2+} (1.12 Å) and Mn^{2+} (0.96 Å) (Shannon, 1976); all are within $\pm 20\%$ size of Ca^{2+} and Mn^{2+} . The Si content of the Al-garnets is close to 3.0 pfu suggesting that the presence of Y and Yb in the garnet cannot be attributed to substitutions $^{8}(\text{Y}, \text{Yb})^{4}(\text{Al}, \text{Fe}^{3+})-(\text{Ca}, \text{Mn})_{-1}\text{Si}_{-1}$ (Jaffe, 1951; Yoder and Keith, 1951; Gentile and Roy, 1960). All garnets are enriched in Mn and Ca (1.7–2.9 pfu in total). These facts and $\text{Na}/(\text{Y} + \text{Yb})$ positive correlation suggest that most of the Na in the Al-garnets enters the structure through the $^{8}(\text{Na})^{8}(\text{Y}, \text{Yb})^{4}(\text{Ca}, \text{Mn})_{-2}$ substitution. On the other hand, the Na content of the Fe^{3+} -garnet is distinctly lower than the Y + Yb content, and the Si content of the Fe^{3+} garnet is usually < 2.97 pfu, suggesting the presence of $^{4}(\text{Fe}^{3+}, \text{Al})$. The excess Y + Yb over Na probably indicates up to 3 mol% of a $(\text{Y}, \text{Yb})_3(\text{Al}, \text{Fe}^{3+})_2(\text{Fe}^{3+}, \text{Al})_3\text{O}_{12}$ component in the Fe^{3+} -garnets.

The $\text{Na}/(\text{Y} + \text{Yb})$ decreases with increasing mean ionic radius of cations (MIR), and the Al-garnets have distinctly higher $\text{Na}/(\text{Y} + \text{Yb})$ than the Fe^{3+} -garnet (Fig. 6). The MIR of the end-members $\text{Na}_{1.5}\text{Y}_{1.5}\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Na}_{1.5}\text{Y}_{1.5}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$, $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$, and $\text{Y}_3\text{Fe}_2^{3+}\text{Fe}_3^{3+}\text{O}_{12}$ are 0.644, 0.671, 0.662, and 0.727 Å, respectively. The Na-Al and Na- Fe^{3+} garnets have a smaller MIR than the Y-Al and Y- Fe^{3+} garnets, respectively. The negative correlation shown in Figure 6 and the comparison of MIR among the end-members imply that a high $(\text{Y}, \text{Yb})-(\text{Al}, \text{Fe}^{3+})$ component in the Fe^{3+} -garnets would be favored by a

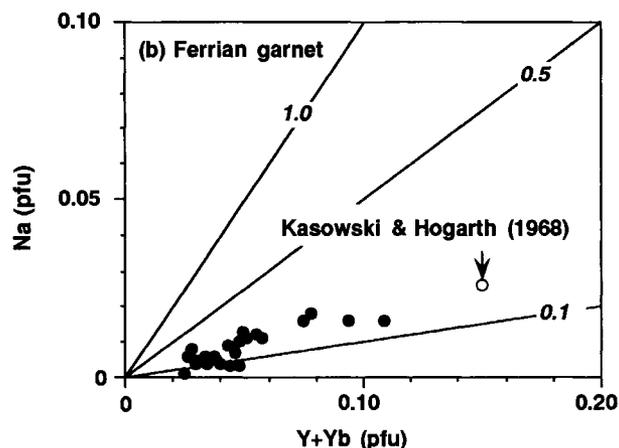
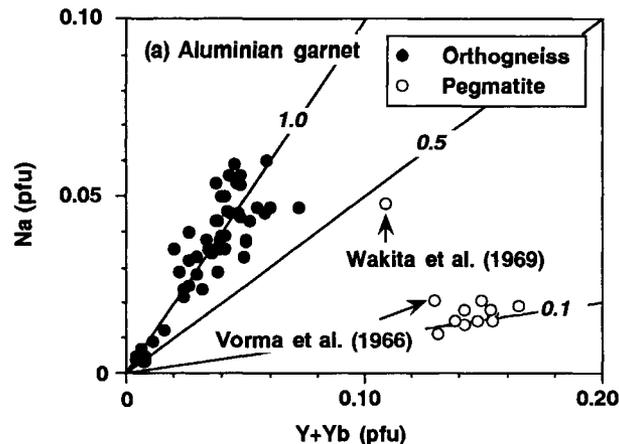


Fig. 7. Compositional ranges of (a) aluminian garnet and (b) ferrian garnet from the Su-Lu orthogneisses (this study) and Y-rich pegmatites (Vorma et al., 1966; Kasowski and Hogarth, 1968; Wakita et al., 1969; this study). Numbers in italics indicate $\text{Na}/(\text{Y} + \text{Yb})$. Abbreviations are defined in Fig. 3.

larger unit cell volume $(12.22 \text{ \AA})^3$ and $(12.376 \text{ \AA})^3$ for $\text{Y}_3\text{Fe}_2^{3+}\text{Al}_{2.5}\text{O}_{12}$ (Gentile and Roy, 1960) and $\text{Y}_3\text{Fe}_2^{3+}\text{Fe}_3^{3+}\text{O}_{12}$ (Geller, 1967), respectively.

Constraints on Na-(Y + Yb) coupled substitution

The Na-Y garnet occurs in mica-poor orthogneisses with subaluminous to alkalic bulk composition. This fact may imply that the Na-(Y + Yb) coupled substitution is favored by high $(\text{Na} + \text{K})/\text{Al}$ environments. The Na-Y garnet, however, occurs even in epidote-bearing orthogneisses, and an alkalic environment may not be essential for garnet to contain $\text{Na}_{1.5}(\text{Y}, \text{Yb})_{1.5}\text{Al}_2\text{Si}_3\text{O}_{12}$ component. Y + Yb content of the Na-Y garnet-bearing orthogneisses is similar to that of ordinary granitic rocks. Thus, unusual Y and Yb enrichments are not necessary for the formation of Na-Y garnet.

The distinct difference of $\text{Na}/(\text{Y} + \text{Yb})$ between the Al- and Fe^{3+} -garnets suggests that the Na-(Y + Yb) substitution is strongly controlled by $X_{\text{Fe}^{3+}}$ and that Al-garnet

probably contains Y and Yb in the form of a $\text{Na}_{1.5}(\text{Y},\text{Yb})_{1.5}\text{Al}_2\text{Si}_3\text{O}_{12}$ component. However, yttrian Al-garnets with low $\text{Na}/(\text{Y} + \text{Yb})$ also occur in Y-rich pegmatites (e.g., Vorma et al., 1966; also cf. Table 2). This fact implies that the Na-(Y + Yb) substitution in garnet may be controlled by pressure-temperature conditions as well as by the Al/Fe^{3+} value and activities of Na and Y + Yb.

Fe^{3+} -garnet in the pegmatites has a $\text{Na}/(\text{Y} + \text{Yb})$ value (0.19) similar to that in the orthogneisses (0.17 ± 0.1) (Fig. 7b). However, the $\text{Na}/(\text{Y} + \text{Yb})$ of most Al-garnets in the pegmatites (usually <0.19) is distinctly lower than that in the orthogneisses (0.99 ± 0.16) (Fig. 7a). The Al-garnets in both pegmatites and orthogneisses coexist with albite (An_{4-5} in pegmatites; Vorma et al., 1966; An_{0-2} in orthogneisses), and thus the difference in $\text{Na}/(\text{Y} + \text{Yb})$ of garnets between the orthogneisses and pegmatites is unlikely to be solely due to differences in Na-activity.

The orthogneisses in the Su-Lu terrane were probably metamorphosed under relatively high-*P* and low-*T* conditions ($T = 400\text{--}500^\circ\text{C}$ and $P = 0.5\text{--}0.7\text{ GPa}$). Liu and Bassett (1986) experimentally showed that Y-Al garnet, $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$, is unstable at high pressures, decomposing into orthorhombic perovskite YAlO_3 , plus the corundum-type sesquioxide Al_2O_3 , at above 7 GPa and 1000 °C. The larger MIR of Y-(Al, Fe^{3+}) garnet also suggests that its formation is favored by lower pressure conditions than Na-Y garnet (cf. Fig. 6). Therefore, the difference in $\text{Na}/(\text{Y} + \text{Yb})$ of garnets between the orthogneisses and pegmatites could be explained mainly as a difference in pressure. Increasing pressure favors incorporation of both Na and Y + Yb in garnet; that is, under the albite-epidote amphibolite facies or higher-pressure conditions Y and Yb are probably incorporated in garnet by $^{81}\text{Na}^{81}(\text{Y},\text{Yb})\text{-(Ca,Mn)}_{-2}$ instead of the $^{81}(\text{Y},\text{Yb})^{81}\text{Al}(\text{Ca,Mn)}_{-1}\text{Si}_{-1}$ substitution effective under lower-pressure conditions.

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REFERENCES CITED

- Banno, S. (1986) Stability of diopside-jadeite solid solution. *Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists*, 81, 281–288 (in Japanese with English abs.).
- Bishop, F.C., Smith, J.V., and Dawson, J.B. (1976) Na, P, Ti and coordination of Si in garnet from peridotite and eclogite xenoliths. *Nature*, 260, 696–697.
- Bureau of Geology and Mineral Resources of Shandong Province (1991) Regional Geology of Shandong Province. In *Geological Memoirs Series 1*, no. 26, 595 p. (in Chinese with English abs.).
- Cong, B., Zhang, R., Li, S., Zhai, M., Wang, S., Chen, C., and Ishiwatari, A. (1992) Preliminary study of isotope chronology of eclogites in northern Jiangsu and eastern Shandong Provinces, China. In *Commemorative Association for Professor Yukio Matsumoto, Ed., Exploration of volcanoes and rocks in Japan, China and Antarctica*, p. 411–417. Semura Furoppi Press, Yamaguchi, Japan.
- Cullers, R.L., and Graf, J.L. (1984) Rare earth elements in igneous rocks of the continental crust: Intermediate and silicic rocks—ore petrogenesis. In P. Henderson, Ed., *Developments in geochemistry*, vol. 2 chapter 8, Rare earth element geochemistry, p. 275–316. Elsevier, Amsterdam.
- Dasgupta, S., Sengupta, P., Guha, D., and Fukuoka, M. (1991) A refined garnet-biotite Fe-Mg exchange geothermometer and its application in amphibolites and granulites. *Contributions to Mineralogy and Petrology*, 109, 130–137.
- Enami, M., Suzuki, K., Zhai, M., and Zheng, X. (1993a) The chemical Th-U-total Pb isochron ages of Jiaodong and Jiaonan metamorphic rocks in the Shandong Peninsula, eastern China. *Island Arc*, 2, 104–113.
- Enami, M., Zang, Q., and Yin, Y. (1993b) High-pressure eclogites in northern Jiangsu—southern Shandong province, eastern China. *Journal of Metamorphic Geology*, 11, 589–603.
- Enami, M., Zhao, Z.Y., and Wang, Q. (1993c) A calderitic garnet paragenesis in granitic gneisses in the Su-Lu ultra high-pressure terrane, eastern China. *Mineralogical Journal*, 16, 268–277.
- Fuhrman, M.L., and Lindsley, D.H. (1988) Ternary-feldspar modeling and thermometry. *American Mineralogist*, 73, 201–215.
- Gasparik, T. (1989) Transformation of enstatite-diopside-jadeite pyroxenes to garnet. *Contributions to Mineralogy and Petrology*, 102, 389–405.
- Geller, S. (1967) Crystal chemistry of the garnets. *Zeitschrift für Kristallographie*, 125, 1–47.
- Gentile, A.L., and Roy, R. (1960) Isomorphism and crystalline solubility in the garnet family. *American Mineralogist*, 45, 701–711.
- Herrmann, A.G. (1970) Yttrium and lanthanides. In K.H. Wedepohl, Ed., *Handbook of geochemistry*, II-5, E-12–15, Springer-Verlag, Berlin.
- Hirajima, T., Zhang, R., Li, J., and Cong, B. (1992) Petrology of the nybôte-bearing eclogite in the Donghai area, Jiangsu Province, eastern China. *Mineralogical Magazine*, 56, 37–46.
- Iimori, T. (1938) Tengerite found in Iisaka and its chemical composition. *Scientific Papers from Institute of Physical and Chemical Research*, 34, 832–841.
- Indares, A., and Martignole, J. (1985) Biotite-garnet geothermometry in the granulite facies: The influence of Ti and Al in biotite. *American Mineralogist*, 70, 272–278.
- Ishiwatari, A., Hirajima, T., Enami, M., Hiramatsu, N., Zaho, Z.Y., Wang, Q., Zhai, M., Cong, B., Zhang, R., Banno, S., and Ishizaka, K. (1992) Eclogites in Shandong Province and Jiangsu Province, China: 1991 survey report. In *Commemorative Association for Professor Yukio Matsumoto, Ed., Exploration of volcanoes and rocks in Japan, China and Antarctica*, p. 393–409. Semura Furoppi Press, Yamaguchi, Japan (in Japanese).
- Jaffe, H.W. (1951) The role of yttrium and other minor elements in the garnet group. *American Mineralogist*, 36, 133–155.
- Kasowski, M.A., and Hogarth, D.D. (1968) Yttrian andradite from the Gatineau Park, Quebec. *Canadian Mineralogist*, 9, 552–558.
- Kawabe, I., Inoue, T., and Kitamura, S. (1994) Comparison of REE analyses of GSJ carbonate reference rocks by ICP-AES and INAA: Fission and spectral interferences in INAA determination of REE in geochemical samples with high U/REE ratios. *Geochemical Journal*, 28, 19–29.
- Kimura, J., Yoshida, T., and Ishikawa, K. (1995) Major and trace element concentrations of Korean geostandard rock samples. *Journal of Mineralogy, Petrology and Economic Geology*, 90, in press (in Japanese with English abs.).
- Kretz, R. (1983) Symbols of rock-forming minerals. *American Mineralogist*, 68, 277–279.
- Liu, K., and Bassett, W.A. (1986) *Elements, oxides, and silicates*, 250 p. Oxford University Press, Oxford, U.K.
- Massonne, H.-J., and Schreyer, W. (1987) Phengite geobarometry based on the limiting assemblage with K-feldspar, phlogopite and quartz. *Contributions to Mineralogy and Petrology*, 96, 212–224.
- Meagher, E.P. (1982) Silicate garnet. In *Mineralogical Society of America Reviews in Mineralogy*, 7, 25–66.
- Moore, R.O., Gurney, J.J., Griffin, W.L., and Shimizu, N. (1991) Ultra-high pressure garnet inclusions in Monastery diamonds: Trace element

- abundance patterns and conditions of origin. *European Journal of Mineralogy*, 3, 213–230.
- Morishita, T., and Suzuki, K. (1993) XRF analyses of the Mitsuhashi granite in the Shitara area, Aichi Prefecture. *Bulletin of the Nagoya University, Furukawa Museum*, no. 9, 77–90 (in Japanese with English abs.).
- Okay, A.I., and Sengör, A.M.C. (1992) Evidence for intracontinental thrust-related exhumation of the ultra-high-pressure rocks in China. *Geology*, 20, 411–414.
- Reid, A.M., Brown, R.W., Dawson, J.B., Whitfield, G.G., and Siebert, J.C. (1976) Garnet and pyroxene compositions in some diamondiferous eclogites. *Contributions to Mineralogy and Petrology*, 58, 203–220.
- Ringwood, A.E., and Lovering, J.F. (1970) Significance of pyroxene-ilmenite intergrowths among kimberlite xenoliths. *Earth and Planetary Science Letters*, 7, 371–375.
- Ringwood, A.E., and Major, A. (1971) Synthesis of majorite and other high pressure garnets and perovskites. *Earth and Planetary Science Letters*, 12, 411–418.
- Schertl, H.-P., Schreyer, W., and Chopin, C. (1991) The pyrope-coesite rocks and their country rocks at Parigi, Dora Maira Massif, Western Alps: Detailed petrography, mineral chemistry and *P-T* path. *Contributions to Mineralogy and Petrology*, 108, 1–21.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sobolev, N.V., and Lavrent'ev, J.G. (1971) Isomorphous sodium admixture in garnets formed at high pressure. *Contributions to Mineralogy and Petrology*, 31, 1–12.
- Thompson, R.N. (1975) Is upper-mantle phosphorus contained in sodic garnet? *Earth and Planetary Science Letters*, 26, 417–424.
- Vorma, A., Ojanperä, P., Hoffrén, V., Siivola, J., and Löfgren, A. (1966) On the rare earth minerals from the Pyörönmaa pegmatite in Kangasala, SW-Finland. *Comptes Rendus de la Société géologique de Finlande*, 38, 241–274.
- Wakita, H., Shibao, K., and Nagashima, K. (1969) Yttrian spessartine from Suishoyama, Fukushima Prefecture, Japan. *American Mineralogist*, 54, 1678–1683.
- Yoder, H.S., and Keith, M.L. (1951) Complete substitution of aluminum for silicon: The system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$. *American Mineralogist*, 36, 519–533.
- Yoshida, T., Matsumoto, K., and Aoki, K. (1986) Photon-activation analysis of standard rocks using an automatic γ -ray counting system with a micro-robot. *Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists*, 81, 406–422.
- Yu, X. (1990) *Geologic Map of China, 1:5,000,000 with explanatory text, 73 p.* Geological Publishing House, Beijing, China (in Chinese).
- Zhang, R., Cong, B., and Liou, Z. (1993) Su-Lu ultrahigh-pressure metamorphic terrane and explanation of its origin. *Acta Petrologica Sinica*, 9, 211–226 (in Chinese with English abs.).

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APPENDIX TABLE 1. Chemical compositions of Na-Y garnet-bearing orthogneisses from the Su-Lu terrane, eastern China

	91TF03a*	91TF03b**	91H01**	91M02**	91TF03a*		91TF03b**		91H01**		91M02**		
					ICP-AES	XRF	PAA	XRF	PAA	XRF	PAA		
	Weight percent				ppm								
SiO ₂	77.56	77.53	77.00	76.73	Y	53	108	111	66	67	44	46	
TiO ₂	0.14	0.15	0.14	0.16	La	52							
Al ₂ O ₃	11.03	11.28	12.75	12.56	Ce	73		132		25		22	
Fe ₂ O ₃ †	2.56	3.03	1.75	1.27	Pr	13	Ba	1137	1110	1722	1591	765	714
MnO	0.12	0.07	0.07	0.04	Nd	50	Co		0.2		0.6		1.8
MgO	0.01	0.03	0.09	0.16	Sm	9.9	Cr		trace				
CaO	0.13	0.22	0.45	0.73	Eu	1.5	Cs		0.66		0.39		0.94
Na ₂ O	4.24	4.25	4.87	3.93	Gd	9.0	Nb	12	15	15	18	12	15
K ₂ O	3.54	3.69	3.46	4.42	Tb	1.5	Ni		1.7				
P ₂ O ₅	0.00	0.00	0.01	0.02	Dy	10	Pb	21		36		9.9	
Total	99.33	100.25	100.59	100.02	Ho	2.1	Rb	79	77	59	59	116	116
					Er	6.6	Sc		2.5		2.0		3.1
					Tm	1.0	Sr	29	33	47	51	76	78
					Yb	7.0	Th	12		27		13	
					Lu	1.0	Zn		86		31		
							Zr	692	680	437	413	140	123

* Analytical methods at Nagoya University are XRF (Morishita and Suzuki, 1993) for major elements, and ICP-AES method coupled with preconcentration procedures (Kawabe et al., 1994) for trace elements.

** Analytical methods at Tohoku and Fukushima Universities are XRF (Kimura et al., 1995) for major elements, and XRF (Kimura et al., 1995) and/or PAA method with high-resolution γ -ray spectrometry (Yoshida et al., 1986) for trace elements.

† Total Fe as Fe₂O₃.