

# Sr-bearing zoisite and epidote in ultra-high pressure (UHP) metamorphic rocks from the Su-Lu province, eastern China: An important Sr reservoir under UHP conditions

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## ABSTRACT

Sr-bearing zoisite and epidote are common constituents of eclogites and associated parashists throughout the Su-Lu ultra-high pressure (UHP) province, eastern China. The SrO content of prograde zoisite and epidote reaches 3.2 wt% in crystal cores and generally decreases toward crystal margins. Retrograde epidote is poorer in SrO (<0.1 wt%). Preliminary rare earth element (REE) analyses of epidote give La<sub>2</sub>O<sub>3</sub> (up to 2.9 wt%), Ce<sub>2</sub>O<sub>3</sub> (5.9 wt%), and Nd<sub>2</sub>O<sub>3</sub> (3.0 wt%). REE contents of zoisite are distinctly lower (La<sub>2</sub>O<sub>3</sub> up to 0.16 wt%, Ce<sub>2</sub>O<sub>3</sub> up to 0.26 wt%, and Nd<sub>2</sub>O<sub>3</sub> up to 0.16 wt%) than coexisting epidote. Apatite is always more depleted in SrO (0.10–0.59 wt% on average) than coexisting zoisite and epidote, and Sr-Ca partition coefficients for zoisite and epidote and apatite [(Sr/Ca)<sub>zo/ep-ap</sub>] range from 5 to 20. SrO content of K-white mica (0.012–0.044 wt%) is an order of magnitude lower than that of apatite. An evaluation of the SrO content in zoisite and epidote and their modal abundances in seven samples indicates that >70% of the whole-rock SrO is contained in these minerals. Apatite and K-white mica are only minor reservoirs for SrO in these rocks. Zoisite and epidote are thus regarded as the most important Sr reservoirs at UHP conditions where calcic plagioclase and titanite are unstable.

## INTRODUCTION

Monoclinic epidote-group minerals have two distinct sites commonly occupied by Ca: ninefold-coordinated A1 and tenfold-coordinated A2 sites. The A2 site is slightly larger than the A1 site, and its size increases with incorporation of Fe<sup>3+</sup> and Mn<sup>3+</sup> in octahedral M1 and M3 sites. The A2 site is too large for Ca (1.23 Å) (Dollase 1971); however this site readily incorporates Sr (1.36 Å) and larger cations. Sr-rich epidote (up to 8.5 wt% SrO: Grapes and Watanabe 1984; Brastad 1985), piemontite (up to 15.1 wt%: Mottana 1986; Perseil 1990), and allanite (1.5 wt%: Exley 1980) have been reported in some metamorphic rocks, manganese deposits, and hydrothermally altered rocks. In contrast, orthorhombic zoisite has two Ca sites of essentially the same size as the A1 site of the monoclinic epidote-group minerals (Dollase 1968). Therefore zoisite contains very little Sr and rare earth elements (REE) when found in normal rock compositions metamorphosed under *P-T* conditions where calcic plagioclase and other phases that favor Sr and REE are stable. However, Sr-rich zoisite (up to 7.4 wt% SrO) has been reported from Sr-metasomatized eclogite (up to 2.4 wt% whole rock SrO) in the Western Gneiss Region of Norway (Brastad 1985). This study (1) reports the common and widespread occurrence of Sr-rich zoisite and epidote (up to 3.2 wt% SrO) in ultra-high pressure (UHP) metamorphic rocks of the Su-Lu province, eastern China, (2) examines the partitioning of Sr among zoisite and epidote and other phases that could incorporate Sr (e.g., apatite and K-white mica), and (3) emphasizes the im-

portance of zoisite and epidote as Sr reservoirs under UHP conditions where calcic plagioclase and titanite are unstable.

## GEOLOGICAL BACKGROUND AND PETROGRAPHY

The Sr-bearing zoisite and epidote studied here occur in eclogites and associated parashists from the Su-Lu UHP province of eastern China, which is an eastern extension of the Dabie UHP province (Fig. 1). Twenty-five samples collected from the seven localities shown in Figure 1 were examined in detail; zoisite, epidote, or both in all samples were confirmed to have >0.5 wt% SrO.

The Su-Lu province is bounded by the Yantai-Qingdao-Wulian (YQW) fault in the northwest (Yu 1990), where it is in contact with middle to late Proterozoic ortho- and paragneisses (730–1620 Ma; Enami et al. 1993a; Ishizaka et al. 1994). The Su-Lu province is underlain chiefly by orthogneisses and amphibolite, in which coesite-eclogite, garnet-peridotite, and marble blocks occur sporadically. The UHP eclogites and associated parashists occur as lenticular blocks 1 to 300 m long, elongate parallel to the foliation of the enclosing country rock gneisses (e.g., Yang 1991; Zhang et al. 1995; Wallis et al. 1997). The peak metamorphic conditions of the UHP rocks are estimated at >2.6 GPa and 700–890 °C (e.g., Enami et al. 1993b; Zhang et al. 1995). The sequence of UHP rocks and the surrounding country rocks were both subjected to greenschist to albite-epidote amphibolite facies metamorphism during the Mesozoic (Cong et al. 1992; Ishiwatari et al. 1992). In the country rocks, no

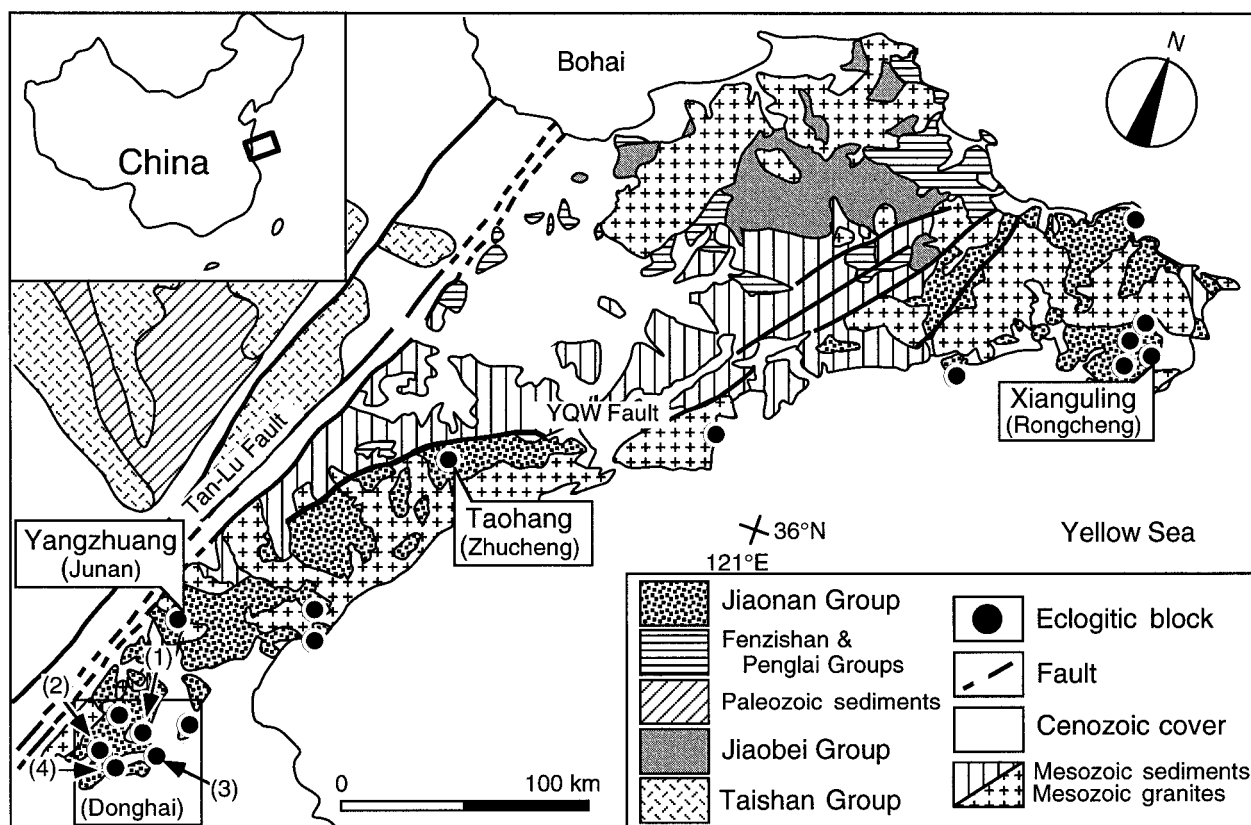


FIGURE 1. Geological sketch map showing sample localities in the northern Jiangsu and southern Shandong Provinces, eastern China. Localities (1), (2), (3), and (4) in the Donghai area correspond to Hetang, Caihu, Quiglongshan, and Maobei, respectively. The other localities include Yangzhuang (Junan), Taohang (Zhucheng), and Xianguling (Rongcheng). Tan-Lu Fault = Tancheng-Lujian fault; YQW Fault = Yantai-Qingdao-Wulian fault. The Jiaobei and Jiaonan Groups are tentative names for the middle Proterozoic and early Mesozoic gneisses, respectively.

clear evidence exists for UHP metamorphism before the greenschist to albite-epidote amphibolite facies event.

Petrological and mineralogical data for UHP rocks in the Su-Lu province are presented by Enami et al. (1993b), Zhang et al. (1995), and others. The eclogites studied consist mainly of garnet, omphacite, silica minerals (quartz  $\pm$  coesite), zoisite and epidote, paragonite, phengite, kyanite, calcic-subcalcic amphiboles, and rutile. Accessory minerals are apatite, titanite, plagioclase, and ilmenite. Paragonite and titanite are retrograde phases that form rims on kyanite and rutile, respectively. Most prograde amphiboles occur as inclusions in garnet. Retrograde amphiboles surround garnet and form symplectites with plagioclase. The parascists have mineral assemblages similar to those of the eclogites, although they contain only a little omphacite but large amounts of quartz (possibly after coesite). Garnet in the parascists is porphyroblastic and reaches 3 mm in diameter. Some garnet and omphacite crystals include coesite and quartz pseudomorphs (Zhang et al. 1995).

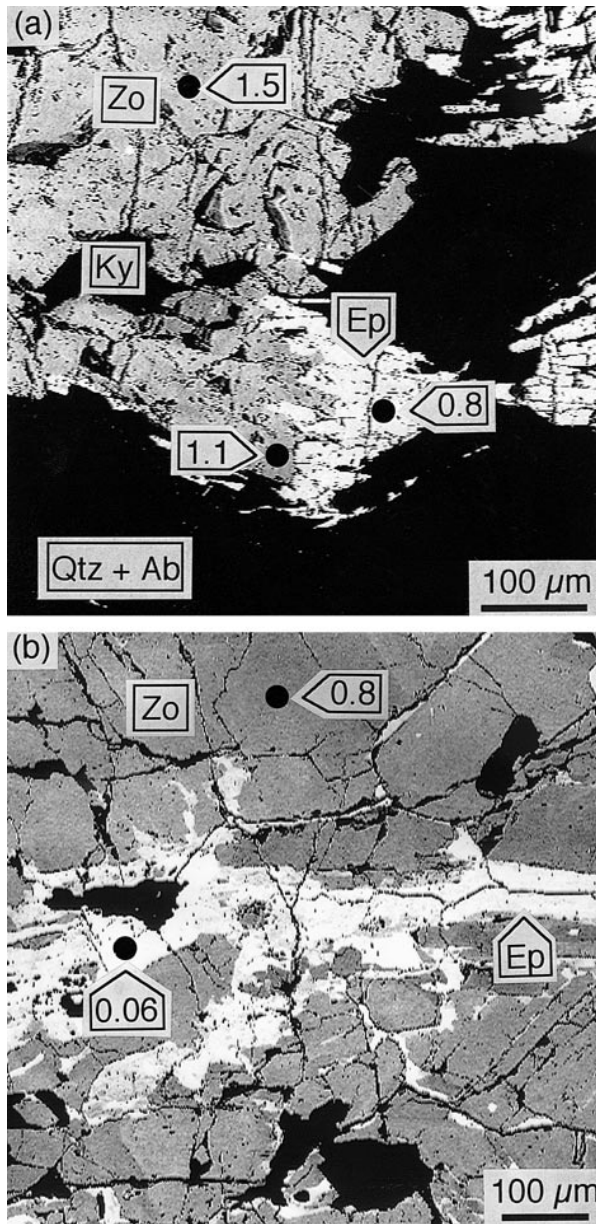
Prograde zoisite and epidote are common interstitial phases between garnet, omphacite, and other prograde UHP minerals. In addition, both minerals occur as inclu-

sions in garnet and omphacite, and therefore they appear to have formed during the same UHP stage. In a Junan sample (SJY02), fine-grained epidote forms an aggregate with hornblende and quartz included in garnet, whereas zoisite occurs in the matrix. The epidote-bearing aggregates might have recrystallized before the matrix zoisite. In a parascist from the Donghai area (91HZ17), epidote always surrounds zoisite (Fig. 2a). In this case, zoisite formed before epidote during the UHP metamorphism. Retrograde epidote occurs as veinlets cutting prograde zoisite in some Junan samples (SD0307, SD0315) (Fig. 2b).

Modal abundances of the principal minerals in seven samples from Yangzhuang were estimated using Al, Ca, and K X-ray mapping data ( $35 \times 25$  mm:  $3.5 \times 10^5$  pixels). Garnet and omphacite abundances are 19–46 and 14–65 vol%, respectively. Zoisite and epidote have non-overlapping abundances of 27–28 and 0–8 vol%, respectively. K-white mica, kyanite, and apatite constitute less than 9, 6, and 0.6 vol% of the rocks, respectively.

#### MINERAL CHEMISTRY

All samples were analyzed on JEOL electron-probe microanalyzers, the JXA-733 (WDS), and the JXA-8800R



**FIGURE 2.** Backscattered-electron images showing textural relationships between zoisite and epidote. (a) Prograde epidote as a rim on zoisite. (b) Retrograde epidote as a veinlet cutting prograde zoisite. Numbers enclosed in polygonal boxes indicate the SrO-content (wt%) of zoisite and epidote. Abbreviations are: Zo = zoisite; Ep = epidote; Ky = kyanite; Qtz = quartz; Ab = albite.

(WDS + EDS) at Nagoya University. Accelerating voltage, specimen current, and beam diameter for quantitative analyses were 15 kV, 12 nA on the Faraday cup, and 3 μm, respectively. The Bence and Albee (1968) method was used for matrix corrections. Representative microprobe analyses of Sr-bearing zoisite, epidote, and coexisting apatite are given in Table 1. The detection limit of SrO is 0.02–0.03 wt% ( $2\sigma$  level) for all minerals. Epidote

incorporates REE (detection limit: 0.03 wt%) by the substitution REE (Mg, Fe<sup>2+</sup>, Mn)Ca<sub>-1</sub>Al<sub>-1</sub> (see below); thus some iron is FeO and Fe<sup>2+</sup> = REE – (Mg + Mn). All iron in zoisite is assumed to be incorporated as Fe<sub>2</sub>O<sub>3</sub>. Sr concentrations of K-white mica were determined by isotope dilution mass spectrometry using the Finnigan MAT THQ at Nagoya University.

#### Zoisite and epidote

Values of  $X_{Fe}$  [= (Fe<sup>3+</sup> + Fe<sup>2+</sup>)/(Al + Fe<sup>3+</sup> + Fe<sup>2+</sup> + Mn + Mg)] for zoisite and epidote are relatively uniform within each sample. Zoisite is always a prograde phase and its  $X_{Fe}$  is 0.04–0.05. Prograde epidote that coexists with zoisite has  $X_{Fe}$  that ranges from 0.11 to 0.14. Epidote in zoisite-free eclogites has variable  $X_{Fe}$ , ranging from 0.12 to 0.24. Retrograde epidote is distinctly richer in Fe<sub>2</sub>O<sub>3</sub> ( $X_{Fe}$  = 0.19 ± 0.01) compared with prograde epidote in the same sample (0.12 ± 0.02). The MnO contents of zoisite and epidote are generally <0.05 and 0.2 wt%, respectively. The MgO content reaches 1.3 wt% in epidote and is typically less than 0.1 wt% in zoisite. The sum of divalent cations (Ca + Sr) in the A1 and A2 sites equals 1.99 ± 0.02 per formula unit (pfu; O = 12.5) for zoisite and 1.94 ± 0.04 pfu for epidote, indicating the simple substitution SrCa<sub>-1</sub>. Some epidotes having low (Ca + Sr) are enriched in Mg + Fe<sup>2+</sup> + Mn (see above). REE are higher in epidote than in coexisting zoisite (up to 2.9 vs. 0.16 wt% La<sub>2</sub>O<sub>3</sub>, up to 5.9 vs. 0.26 wt% Ce<sub>2</sub>O<sub>3</sub>, and up to 3.0 vs. 0.16 wt% Nd<sub>2</sub>O<sub>3</sub>).

Figure 3 shows variations of SrO in zoisite and epidote. Most zoisite and epidote crystals are zoned with decreasing SrO toward crystal margins (Fig. 4). The cores of zoned grains contain up to 3.2 wt% SrO in zoisite and up to 2.7 wt% SrO in epidote. The SrO content of epidote correlates with its mode of occurrence; e.g., in samples SD0307 and SD0315 primary epidote (0.7 ± 0.3 wt%) contains more SrO than secondary epidotes from veins (0.06 ± 0.01 wt%; Fig. 5).

#### Other minerals

Sr was not detected in garnet and omphacite by EPMA. Garnets are Mn-poor almandine-pyrope-grossular types, and their average compositions are Alm<sub>43-51</sub>Sps<sub>01-02</sub>Prp<sub>14-30</sub>Grs<sub>23-33</sub> in eclogites and Alm<sub>40-49</sub>Sps<sub>01</sub>Prp<sub>20-33</sub>Grs<sub>26-30</sub> in parascists [abbreviations follow Kretz (1983)]. The garnets typically contain up to 0.03 wt% Na<sub>2</sub>O implying an NaTiCa<sub>-1</sub>Al<sub>-1</sub> substitution (cf. Enami et al. 1995; Kato et al. 1997).

Omphacites in most samples are relatively poor in Fe<sub>2</sub>O<sub>3</sub> (generally less than 1.0 wt%), and their average compositions are Aug<sub>31-51</sub>Jd<sub>46-62</sub>Acm<sub>0-7</sub> in eclogites and Aug<sub>47</sub>Jd<sub>53</sub>Acm<sub>00</sub> in parascists. In one Donghai sample (91Q03), acmite-rich omphacite (Aug<sub>35</sub>Jd<sub>47</sub>Acm<sub>17</sub>) coexists with Fe<sub>2</sub>O<sub>3</sub>-rich epidote ( $X_{Fe}$  = 0.24 ± 0.01).

Prograde amphiboles are mostly pargasite with Si = 6.6–6.7 pfu (O = 23) and  $X_{Mg}$  [=Mg/(Mg + Fe<sup>2+</sup>)] = 0.59–0.80. Nyböite also occurs as a prograde phase in zoisite-free eclogites. Some prograde amphiboles in the Donghai samples contain up to 2.8 wt% Cl. Retrograde

TABLE 1. Representative analyses of zoisite, epidote, and apatite

	Donghai						Junan						Rongcheng	
	91CH08b (Ec)			91HZ17 (Ps)			SD0307 (Ec)			SJY02 (Ec)			R1-7 (Ec)	
	Zo	Ep	Ap	Zo	Ep		Zo	Ep	Ap	Zo	Ep	Ap	Ep	Ap
<b>Weight percentages</b>														
SiO <sub>2</sub>	38.4	37.6		38.5	37.9		38.8	37.2		38.7	37.8		36.2	
TiO <sub>2</sub>	0.11	0.06		0.17	0.25		0.00	0.05		0.08	0.14		0.08	
Al <sub>2</sub> O <sub>3</sub>	31.1	28.4		31.3	27.5		31.4	27.1		31.3	28.7		26.5	
Cr <sub>2</sub> O <sub>3</sub>	0.2	0.04		0.13	0.01		0.00	0.00		0.14	0.07		0.00	
Fe <sub>2</sub> O <sub>3</sub> *	2.14	5.09	0.10†	2.14	7.64		2.05	6.22	0.12†	1.91	6.06	0.13†	5.66	0.07†
MnO	0.03	0.04	0.02	0.00	0.15		0.00	0.00	0.02	0.00	0.06	0.00	0.14	0.00
MgO	0.00	0.14	0.08	0.02	0.06		0.00	0.38	0.00	0.04	0.11	0.05	0.83	0.00
SrO	1.20	2.66	0.14	1.54	0.64		1.31	0.94	0.15	3.04	1.67	0.43	0.93	0.66
CaO	23.1	22.0	55.1	23.3	23.3		23.4	21.1	54.8	22.4	22.6	54.1	19.3	55.3
La <sub>2</sub> O <sub>3</sub>	b.d.			b.d.	b.d.		b.d.	0.71		b.d.	0.08	0.06	1.49	0.04
Ce <sub>2</sub> O <sub>3</sub>	0.14			b.d.	0.06		0.12	1.60		0.05	0.15	b.d.	3.62	0.07
Nd <sub>2</sub> O <sub>3</sub>	0.08			b.d.	b.d.		0.06	0.94		0.08	0.13	b.d.	2.19	0.14
P <sub>2</sub> O <sub>5</sub>			41.9						41.6			41.8		40.9
F			3.03						2.77			3.75		3.73
Cl			0.01						0.13			0.06		0.00
Less O = F + Cl			1.28						1.20			1.59		1.57
Total	96.5	96.0	99.1	97.1	97.5		97.1	96.2	98.4	97.7	97.6	98.7	96.9	99.3
<b>Formula proportion§</b>														
Si	2.996	3.000		2.988	2.979		3.006	3.008		3.003	2.970		2.984	
Ti	0.006	0.004		0.010	0.015		0.000	0.003		0.005	0.008		0.005	
Al	2.860	2.671		2.863	2.548		2.867	2.583		2.863	2.658		2.574	
Cr	0.012	0.003		0.008	0.001		0.000	0.000		0.009	0.004		0.000	
Fe <sup>3+</sup> ‡	0.126	0.306		0.125	0.452		0.119	0.329		0.112	0.358		0.244	
Fe <sup>2+</sup> ‡		0.000	0.007		0.000			0.050	0.009		0.000	0.009	0.102	0.005
Mn	0.002	0.003	0.001	0.000	0.010		0.000	0.000	0.001	0.000	0.004	0.000	0.010	0.000
Mg	0.000	0.017	0.010	0.002	0.007		0.000	0.046	0.000	0.005	0.013	0.006	0.102	0.000
Sr	0.054	0.123	0.007	0.069	0.029		0.059	0.044	0.007	0.137	0.076	0.021	0.044	0.032
Ca	1.931	1.881	4.982	1.938	1.962		1.942	1.828	4.990	1.863	1.903	4.944	1.704	5.021
La	b.d.			b.d.	b.d.		b.d.	0.021		b.d.	0.002	0.002	0.045	0.001
Ce	0.004			0.001	0.002		0.003	0.047		0.001	0.004	b.d.	0.109	0.002
Nd	0.002			b.d.	b.d.		0.002	0.027		0.002	0.004	b.d.	0.064	0.004
P			2.993						2.993			3.018		2.935
F			0.809						0.745			1.012		1.000
Cl			0.002						0.019			0.009		0.000

Note: Abbreviations are Ec = eclogite; Ps = parashist; Zo = zoisite; Ep = epidote; Ap = apatite; b.d. = below detection limit.

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.

† Total Fe as FeO.

‡ Calculated values (see text).

§ Based on 12.5 O atoms for zoisite and epidote, and 8 cations for apatite.

amphiboles have variable compositions. Pargasite from symplectites has Si = 6.1–6.3 pfu and  $X_{Mg}$  = 0.62–0.82, whereas amphibole replacing garnet is characteristically low in Si (5.6–5.8 pfu).

Potassium-white micas are phengitic, and their average Si contents and  $X_{Na}$  [=Na/(Na + K + Ba + Ca)] are 3.3–3.4 pfu (O = 11) and 0.07–0.10, respectively. SrO concentrations of K-white mica in five samples from Yangzhuang are 0.012–0.044 wt%. Apatite is F-rich (~2.0–3.8 wt% F and <0.7 Cl wt%) and contains ~0.10–0.59 wt% SrO. La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, and Nd<sub>2</sub>O<sub>3</sub> of apatite are <0.06, 0.12, and 0.14 wt%, respectively. Retrograde plagioclase is albitic, (~An<sub>8</sub> to An<sub>15</sub>). The average SrO content of plagioclase is 0.05–0.15 wt%, which is distinctly lower than that of zoisite and epidote. Retrograde titanite contains a small amount of Al<sub>2</sub>O<sub>3</sub> (up to 0.5 wt%), and its contents of SrO and F are <0.1 and 0.2 wt%, respectively.

## DISCUSSION

### SrO contents of zoisite and epidote

Epidote is generally enriched in Sr compared with coexisting zoisite, as shown by Brastad (1985). However, the Sr/Ca values of coexisting zoisite and epidote in the samples of the present study (Fig. 5) are more complex than expected from crystal chemistry, which is most likely due to their variable timing of crystallization. Epidote in sample 91HZ17, for example, has a slightly lower Sr/Ca value than zoisite. The Sr-poorer epidote occurs as a rim on the zoisite and is inferred to be younger. This indicates that Sr was preferentially incorporated into the zoisite during the prograde stage and that epidote crystallized later under Sr-depleted conditions. The gradual Sr decrease toward the margin of the zoisite and epidote supports this interpretation. In sample 91CH08b, the Sr/Ca value of the epidote varies from grain to grain even within a single thin section, and some epidote grains have

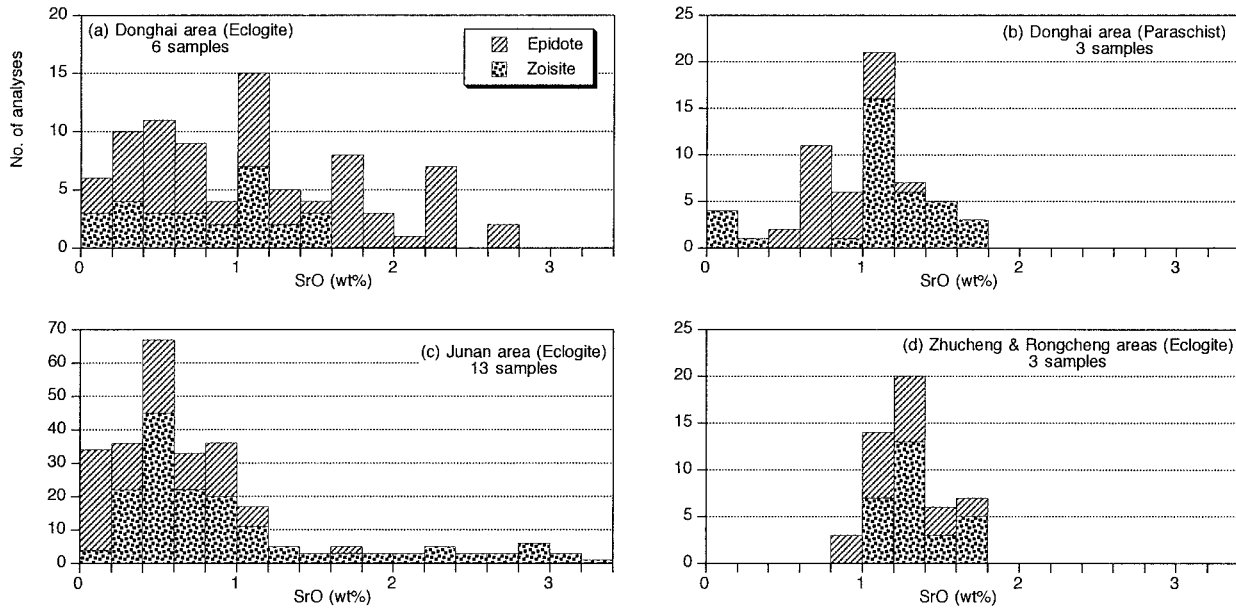
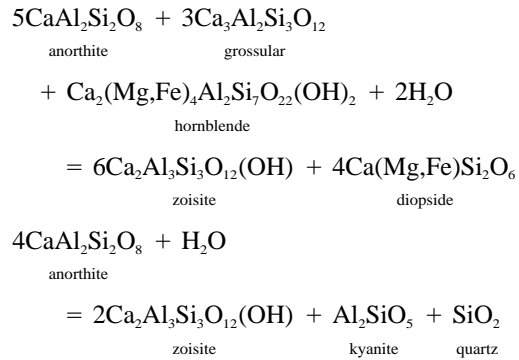


FIGURE 3. Histograms of SrO concentrations (wt%) in zoisite and epidote from eclogite and paraschist.

lower Sr/Ca than zoisite. This Sr heterogeneity of epidote and zoisite might reflect local variations in the SrO content of the protolith. Epidote in SJY02 occurs as aggregate inclusions with hornblende in garnet and has a lower Sr/Ca value than the zoisite in the matrix. Epidote-amphibolite and amphibolite facies assemblages formed prior to the UHP stage are preserved as inclusions in garnet (e.g., Enami et al. 1993b; Zhang et al. 1995). Sr is incorporated preferentially into the calcic plagioclase of

those earlier assemblages, and thus the Sr-poor epidote in SJY02 might be a relic of that earlier stage. Orthorhombic zoisite is a higher-temperature polymorph of the monoclinic phase (Enami and Banno 1980), and the more Sr-rich zoisite in SJY02 might have been formed by the following pressure-sensitive, plagioclase-consuming reactions during high  $P$ - $T$  prograde stage:



#### Sr reservoirs

Sr-partitioning among minerals in medium- to high-pressure metamorphic rocks has been discussed by Sorensen and Grossman (1989), Getty and Selverstone (1994), Hickmott et al. (1992), and others. Sorensen and Grossman (1989) studied clinopyroxene-bearing garnet-amphibolites migmatized to varying degrees in the Catalina Schist, southern California. Their data clearly indicate that Sr preferentially concentrates in zoisite and epidote of non-migmatized amphibolites, but is enriched in calcic plagioclase, apatite, and titanite by the breakdown of zoisite and epidote during migmatization. Geochemical studies on banded eclogites from the Tauern Windows, eastern Alps, by Getty and Selverstone (1994) showed

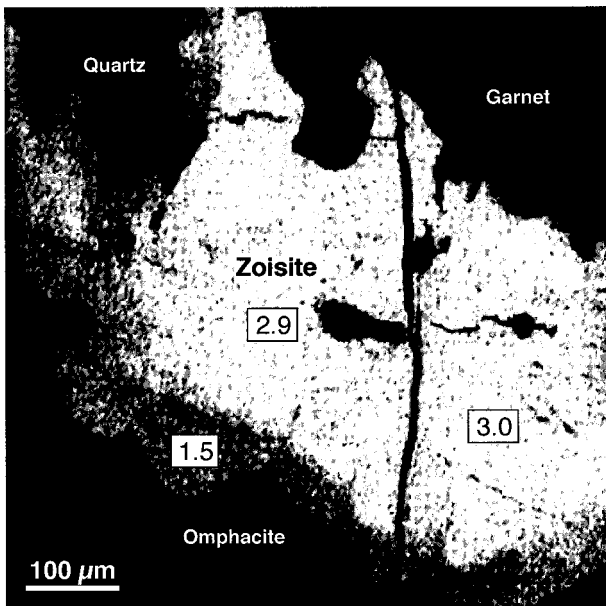


FIGURE 4. Strontium X-ray map of zoisite in eclogite. Brighter shades indicate higher Sr-content. Numbers enclosed in rectangular boxes indicate SrO contents (wt%).

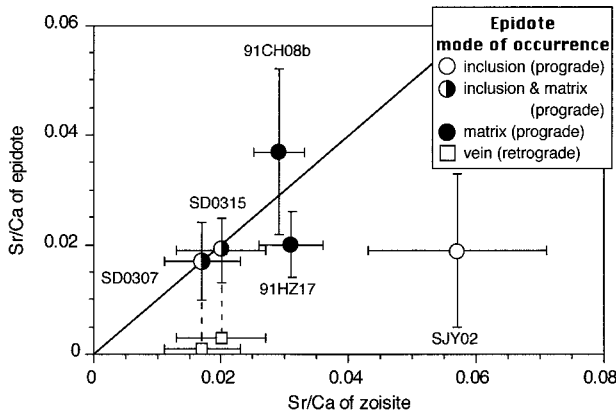


FIGURE 5. Sr-Ca partitioning between coexisting zoisite and epidote. Zoisites are all prograde crystals in matrix. Data points represent average values  $\pm 1\sigma$ .

that zoisite and epidote contain up to 0.25 wt% SrO and that there is little systematic partitioning of trace elements (including Sr) among garnet, omphacite, and zoisite and epidote. They emphasized that mineral-fluid interactions along grain boundaries largely control trace element behavior during eclogite facies metamorphism.

The SrO analyses of major minerals in the Su-Lu UHP rocks demonstrate that zoisite and epidote, and apatite, are also the major Sr-bearing phases under UHP conditions. Zoisite and epidote are always richer in SrO than coexisting apatite, and Sr-Ca partition coefficients between these phases  $[(Sr/Ca)_{zo/ep-ap}]$  range from 5 to 20 (Fig. 6). SrO contents of K-white mica (0.012–0.044 wt%) are an order of magnitude lower than those of apatite (0.10–0.59 wt%). The estimated  $(Sr/Ca)_{zo/ep-ap}$  values in the Su-Lu samples are consistent with those reported for the Catalina Schist (5.2–5.3; Sorensen and Grossman 1989). The ionic radius of Sr might be too large to be accepted readily in the sevenfold- and ninefold-coordinated Ca sites of apatite (Brastad 1985). A positive relationship between whole-rock SrO content and the modal abundance of zoisite and epidote in eclogites from an outcrop at Yangzhuang, Junan area, (Fig. 7a) implies that SrO content of the eclogites is strongly controlled by the abundance of zoisite and epidote. Mass-balance calculations for seven samples reveals that >70% of the whole-rock SrO is bound in these minerals (Fig. 7b). Apatite and K-white mica are only minor reservoirs for SrO in these rocks. Sorensen and Grossman (1989) estimated that (1) about 85% of the SrO in the Catalina Schist amphibolites is concentrated in zoisite and (2) the contribution of apatite to the SrO budget of the whole rock is about one thirtieth that of zoisite. The higher SrO contents and modal abundances of zoisite and epidote in comparison with apatite and K-white mica imply that zoisite and epidote are the most important Sr reservoirs under HP and UHP conditions where calcic plagioclase and titanite are unstable. Although no reports exist of Sr-bearing minerals from the Su-Lu and Dabie UHP prov-

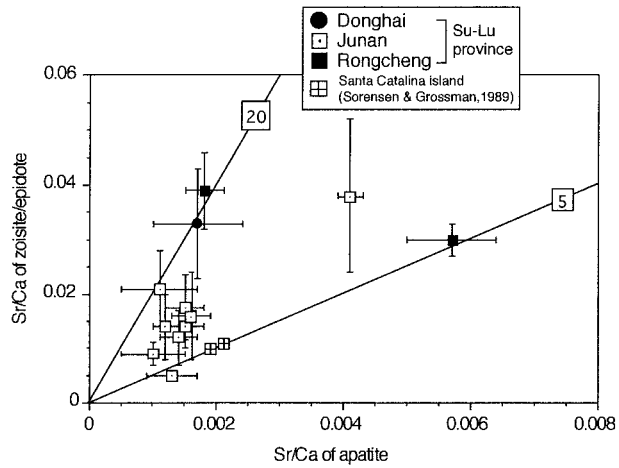


FIGURE 6. Sr-Ca partitioning between coexisting zoisite and epidote and apatite. Numbers enclosed in rectangular boxes indicate the Sr-Ca partition coefficient. Data points represent average values  $\pm 1\sigma$ .

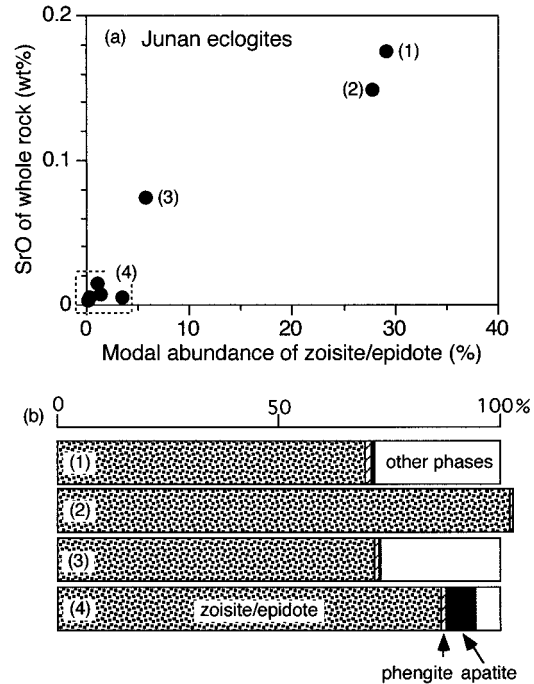


FIGURE 7. Relationships between whole-rock SrO contents and modal abundances of zoisite and epidote (a) and calculated strontium "budgets" (b) of eclogites from an outcrop at Yangzhuang, Junan area (see Fig. 1). Bar lengths represent the fraction (wt%) of the whole rock concentration of SrO present in each mineral. The SrO "budget" of sample (2) is over 100%, which is a result of uncertainties in the mass-balance calculations. SrO content of whole rocks was determined by XRF analysis at Nagoya University (Morishita and Suzuki 1993).

inces, Ca-poor, possibly Sr-rich zoisite and epidote have been reported (e.g., Hirajima et al. 1992; Zhang and Liou 1994; Okay 1995). Thus, the occurrences of Sr-bearing zoisite and epidote in the UHP provinces may be widespread, and the presence or absence of these phases may strongly control the cycling of Sr in deep crustal environments.

A recent experimental study in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system under high-pressure conditions indicates that zoisite and lawsonite are stable at up to 6.7 and 9.2 GPa, respectively, at about  $T = 1000$  °C (Schmidt and Poli 1994). Thus, zoisite and lawsonite appear to be major Ca-Al silicates within subduction zones, even at depths of >150 km. Lawsonite coexisting with epidote in high  $P$ - $T$  Sanbagawa metamorphic rocks contains up to 0.3 wt% SrO with Sr-Ca partition coefficients between these two phases  $[(\text{Sr}/\text{Ca})_{\text{law-ep}}]$  ranging from 0.7 to 1.1 (M. Enami, unpublished data). These data imply that lawsonite is a possible alternative Sr reservoir at depths of >200 km where zoisite is unstable. Hickmott et al. (1992) pointed out that dehydration and melting of epidote-group minerals occurs in a depth range similar to that of the Wadachi-Benioff zone underlying island-arc volcanic fronts (typically ~100 km), and that the released Sr-rich fluid leads to the high Sr abundances of arc magmas. The high-pressure stability of zoisite and lawsonite, however, implies that these minerals could contribute considerably to the Sr budget of subducted slabs and that Sr could be transported efficiently to depths of more than 200 km.

### Implications for Rb-Sr isotope systematics

Zoisite and epidote contain little Rb, which has a distinctly large ionic radius (1.66 Å for tenfold-coordination; Shannon 1976), and have very low Rb/Sr values (about 10<sup>-4</sup>; Griffin and Brueckner 1985). Consequently, the <sup>87</sup>Sr/<sup>86</sup>Sr value of Sr-rich zoisite and epidote should change very little from its initial value. The <sup>87</sup>Sr/<sup>86</sup>Sr of Sr-rich zoisite and epidote may therefore be a good indicator of initial <sup>87</sup>Sr/<sup>86</sup>Sr and a useful check on the heterogeneity (or homogeneity) of whole rocks during metamorphism. Moreover, the <sup>87</sup>Sr/<sup>86</sup>Sr values of zoisite and epidote should also be important for the calculation of Rb-Sr mineral isochron ages.

### ACKNOWLEDGMENTS

This paper is the result of a cooperative project between Kyoto University, Japan, and the Institute of Geology and Academia Sinica, China; funded by the Japanese Society for the Promotion of Science. We are grateful to T. Hirajima, A. Ishiwatari, M. Zhai, and other members of the project for their frank discussions during the field work. Laboratory works were supported in part by Grants in Aid for Scientific Research from Ministry of Education of Japan (Nos. 06302031 and 08304034). This paper benefited from the critical reviews of B.R. Hacker and an anonymous referee and constructive comments of S.R. Wallis and G.E. Bebout. Our thanks also to S. Yogo for making many thin sections and to Y. Asahara and T. Morishita for their help in chemical analyses by isotope dilution and XRF methods. The loan of four samples (SD0307, SD0315, SJY02, and R1-7) by Q. Zang is gratefully acknowledged.

### REFERENCES CITED

- Bence, A.E. and Albee, A.L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *Journal of Geology*, 76, 382–403.
- Brastad, K. (1985) Sr metasomatism, and partition of Sr between the mineral phases of a meta-eclogite from Bjørkedalen, west Norway. *Tschermak Mineralogische und Petrographische Mitteilungen*, 34, 87–103.
- 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.
- Dollase, W.A. (1968) Refinement and comparison of the structures of zoisite and clinozoisite. *American Mineralogist*, 53, 1882–1898.
- (1971) Refinement of the crystal structures of epidote, allanite and hancockite. *American Mineralogist*, 56, 447–464.
- Enami, M. and Banno, S. (1980) Zoisite-clinozoisite relations in low- to medium-grade high-pressure metamorphic rocks and their implications. *Mineralogical Magazine*, 43, 1005–1013.
- 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. *The 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., Cong, B., Yoshida, T., and Kawabe, I. (1995) A mechanism for Na incorporation in garnet: An example from garnet in orthogneiss from the Su-Lu terrane, eastern China. *American Mineralogist*, 80, 475–482.
- Exley, R.A. (1980) Microprobe studies of REE-rich accessory minerals: Implications for Skye granite petrogenesis and REE mobility in hydrothermal systems. *Earth and Planetary Science Letters*, 48, 97–110.
- Getty, S.R. and Selverstone, J. (1994) Stable isotopic and trace element evidence for restricted fluid migration in 2 GPa eclogites. *Journal of Metamorphic Geology*, 12, 747–760.
- Grapes, R. and Watanabe, T. (1984) Al-Fe<sup>3+</sup> and Ca-Sr<sup>2+</sup> epidotes in metagreywacke-quartzofeldspathic schist, Southern Alps, New Zealand. *American Mineralogist*, 69, 490–498.
- Griffin, W.L. and Brueckner, H.K. (1985) REE, Rb-Sr and Sm-Nd studies of Norwegian eclogites. *Chemical Geology*, 52, 249–271.
- Hickmott, D.D., Sorensen, S.S., and Rogers, P.S.Z. (1992) Metasomatism in a subduction complex: Constraints from microanalysis of trace elements in minerals from garnet amphibolite from the Catalina Schist. *Geology*, 20, 347–350.
- Hirajima, T., Zhang, R., Li, J.J., and Cong, B. (1992) Nyböite from the Donghai area, Jiangsu Province, eastern China. *Mineralogical Magazine*, 56, 37–46.
- Ishiwatari, A., Hirajima, T., Enami, M., Hiramatsu, N., Zhao, 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 (in Japanese).
- Ishizaka, K., Hirajima, T., and Zheng, X. (1994) Rb-Sr dating for the Jiaodong gneiss of the Su-Lu ultra-high pressure province, eastern China. *The Island Arc*, 3, 232–241.
- Kato, T., Enami, M., and Zhai, M. (1997) The ultrahigh-pressure (UHP) marble and eclogite in the Su-Lu UHP terrane, eastern China. *Journal of Metamorphic Geology*, 15, 169–182.
- Kretz, R. (1983) Symbols of rock-forming minerals. *American Mineralogist*, 68, 277–279.
- Morishita, T. and Suzuki, K. (1993) XRF analyses of the Mitsuhashi granite in the Shitara area, Aichi Prefecture. *Bulletin Nagoya University. Furukawa Museum*, No. 9, 77–90 (in Japanese with English abstract).
- Mottana, A. (1986) Blueschist-facies metamorphism of manganiferous schists: A review of the alpine occurrences. In B.W. Evans and E.H.

- Brown, Eds., *Blueschists and Eclogites*, p. 267–299. Geological Society of America Memoir 164.
- Okay, A. (1995) Paragonite eclogites from Dabie Shan, China: Re-equilibration during exhumation? *Journal of Metamorphic Geology*, 13, 449–460.
- Perseil, E.A. (1990) Sur la présence du strontium dans les minéralisations manganésifères de Falotta et de Parssettens (Grisons-Suisse)—Evolution des paragenèses. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 70, 315–320.
- Schmidt, M.W. and Poli, S. (1994) The stability of lawsonite and zoisite at high pressures: Experiments in CASH to 92 kbar and implications for the presence of hydrous phases in subducted lithosphere. *Earth and Planetary Science Letters*, 124, 105–118.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sorensen, S.S. and Grossman, J.N. (1989) Enrichment of trace elements in garnet amphibolites from a paleo-subduction zone: Catalina Schist, southern California. *Geochimica et Cosmochimica Acta*, 53, 3155–3177.
- Wallis, S.R., Ishiwatari, A., Hirajima, T., Ye, K., Guo, J., Nakamura, D., Kato, T., Zhai, M., Enami, M., Cong, B., and Banno, S. (1997) Occurrence and field relationships of UHP meta-granitoid and coesite eclogite in the Su-Lu terrane, eastern China. *Journal of Geological Society of London*, 154, 45–54.
- Yang, J. (1991) Eclogites, garnet pyroxenites and related ultrabasics in Shandong and northern Jiangsu of east China, p. 99. Geological Publishing House, Beijing (in Chinese with English abstract).
- Yu, X. (1990) Geologic Map of China, 1: 5,000,000 with explanatory text, p. 73. Geological Publishing House, Beijing (in Chinese).
- Zhang, R. and Liou, J.G. (1994) Coesite-bearing eclogite in Henan Province, central China: Detailed petrography, glaucophane stability and P-T path. *European Journal of Mineralogy*, 6, 217–233.
- Zhang, R., Hirajima, T., Banno, S., Cong, B., and Liou, J.G. (1995) Petrology of ultrahigh-pressure rocks from the southern Su-Lu region, eastern China. *Journal of Metamorphic Geology*, 13, 659–675.

MANUSCRIPT RECEIVED OCTOBER 15, 1997

MANUSCRIPT ACCEPTED NOVEMBER 5, 1997