Epidote-(Sr), CaSrAl₂Fe³⁺(Si₂O₇)(SiO₄)(OH), a new mineral from the Ananai mine, Kochi Prefecture, Japan

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Epidote-(Sr), CaSrAl₂Fe³⁺(Si₂O₇)(SiO₄)(OH), the Sr-analog of epidote, was found in the Nagakawara and Hohnomori deposits at the Ananai mine, Kochi Prefecture, Japan. It occurs in the form of prismatic crystals up to 1 cm in length in the tinzenite veins or the fine crystal aggregates in piemontite breccia. Epidote-(Sr) is optically biaxial negative, $\alpha = 1.737(2)$, $\beta = 1.780(2)$, $\gamma = 1.792(2)$, and $2V_{calc} = 62^{\circ}$ and has perfect cleavage parallel to {001}. It exhibits pleochroism—*X*: pale greenish yellow, and *Y* and *Z*: pale reddish brown to brownish pink. Its calculated density is 3.74 g/cm^3 , and it has a Mohs' hardness of 6.5. The representative empirical formula of epidote-(Sr) from the Nagakawara deposit is $(Ca_{1.10}Sr_{0.90})_{\Sigma 2.00}$ (Al_{1.92}Fe³⁺_{0.87}Mn³⁺_{0.20})_{S2.99}Si_{3.01}O₁₂(OH) on the basis of OH = 1 and O = 12 per formula unit. The mineral is monoclinic with a space group of $P2_1/m$, a = 8.928 (5), b = 5.652(1), c = 10.244(5) Å, $\beta = 114.46(4)^{\circ}$, V = 470.5(3) Å³, and Z = 2. The strongest seven lines in the X-ray powder diffraction pattern [*d in* Å (*I*/*I*₀) (*hkl*]] were 2.92 (100) (11-3), 2.58 (49) (202), 3.50 (42) (21-1), 2.61 (42) (31-1), 2.72 (41) (013), 2.83 (32) (020), and 3.26 (23) (201). Epidote-(Sr) from the Nagakawara deposit may have been formed from the residual hydrothermal fluid after the crystallization of tinzenite.

Keywords: Epidote-(Sr), Sr-analogue of epidote, Ananai mine, Kochi, Japan

INTRODUCTION

Epidote-group minerals, which have the general formula of $A_2M_3(T_2O_7)(TO_4)(OH)$, are divided into three subgroups: clinozoisite, allanite, and dollaseite subgroups (Armbruster et al., 2006). In the clinozoisite subgroup minerals, divalent cations occupy ninefold-coordinated A(1) and tenfold-coordinated A(2) sites, and trivalent cations occupy sixfold-coordinated M(1), M(2), and M(3)sites. Epidote belonging to the clinozoisite subgroup has the general formula of Ca₂Al₂Fe³⁺(Si₂O₇)(SiO₄)(OH) where Fe³⁺ occupy the M(3) site. The clinozoisite subgroup minerals are classified according to the cation occupancies in the A(2), M(1), and M(3) sites. Piemontite-(Sr), manganipiemontite-(Sr), and clinozoisite subgroup minerals with the A(2) site occupied by Sr (Bonazzi et al., 1990; Armbruster et al., 2002, Miyajima et al., 2003) (Table 1). Sr-bearing epidote has been reported to be found in the Southern Alps, New Zealand (Grapes and Watanabe, 1984); the Motagua fault zone, Guatemala (Harlow, 1994); the Su-Lu province, eastern China (Nagasaki and Enami, 1998); and the Itoigawa-Ohmi district, Japan (Miyajima et al., 2003). Epidote is an important Sr reservoir in the metamorphic rocks (e.g., Nagasaki and Enami, 1998).

The Sr-analog of epidote, CaSrAl₂Fe³⁺(Si₂O₇)(SiO₄) (OH), has been proposed as a possible member of the clinozoisite subgroup minerals by Armbruster et al. (2006). Although Miyajima et al. (2003) have already reported the CaSrAl₂Fe³⁺(Si₂O₇)(SiO₄)(OH) composition as the most Sr-rich niigataite, little has been known about the mineralogical feature of the Sr-analogue of epidote. We also found the Sr-bearing epidote in the Ananai mine, Kochi Prefecture, Japan, and identified this mineral to be similar to epidote-(Sr) proposed by Armbruster et al. (2006). The new mineral data and its name "epidote-(Sr)" have been approved by the Commission on New Minerals

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	-	-	-				
New name	Old name	A1	A2	M1	M2	M3	Reference
Clinozoisite-(Sr)	Niigataite	Ca	Sr	Al	Al	Al	Miyajima et al. (2004)
Epidote-(Sr)	-	Ca	Sr	Al	Al	Fe ³⁺	This study
Ferriepidote-(Sr)	-	Ca	Sr	Fe ³⁺	Al	Fe ³⁺	-
Vanadoepidote-(Sr)	-	Ca	Sr	V^{3+}	Al	Fe ³⁺	-
Mukhinite-(Sr)	-	Ca	Sr	Al	Al	V^{3+}	-
Piemontite-(Sr)	Strontiopiemontite	Ca	Sr	Al	Al	Mn^{3+}	Bonazzi et al. (1990)
Manganipiemontite-(Sr)	Tweddillite	Ca	Sr	Mn ³⁺	Al	Mn ³⁺	Armbruster et al. (2002)

Table 1. Sr-analog of the clinozoisite subgroup minerals proposed by Armbruster et al. (2006)



Figure 1. Location map of the manganese deposits at the Ananai mine. Epidote-(Sr) was found in the Nagakawara and Hohnomori deposits.

and Mineral Names, International Mineralogical Association (#2006-055). A type specimen of the epidote-(Sr) has been deposited in the museum at the Hokkaido University, Sapporo, Japan (#Mineral-07400). Here, we describe the new Sr-analogue of epidote, epidote-(Sr).

ORE MINERALIZATION AND OCCURRENCE

The Ananai mine is located near the Ananaigawa Dam (Fig. 1) and belongs to the Kamiyagawa formation of the northern Chichibu belt that is metamorphosed under prehnite-pumpellyite to partly pumpellyite-actinolite facies. The Ananai mine consists of a gathering of small-scale deposits such as Hohnomori, Fukinaro, Nagakawara, and Matukabe deposits that are located within several square kilometres. These deposits embed lenticular ore bodies in a red metachert and a basaltic green rock characteristically composed of albite, hematite, andradite, aegirine, actinolite, prehnite, chlorite, and calcite. The ore minerals and the stratigraphy of the Ananai mine have been summarized by Yoshimura (1967, 1969). The major mineral assemblage of the ore minerals at the initial stage is braunite + caryopilite \pm quartz that forms a massive and a banded ore in the reddish chert. Siliceous ores with quartz generally consist of rhodonite ± natronambulite assemblage and are often replaced by a so-called chocolate ore with hausmannite + rhodochrosite + tephroite \pm gageite \pm alleghanyite assemblages under low-grade regional metamorphism (e.g., Minakawa, 1998). At the final stage of



Figure 2. Images of epidote-(Sr). (a) The radial aggregate in tinzenite from the Nagakawara deposit. (b) The epidote-(Sr) bearing breccia from the Hohnomori deposit. Ep-Sr, epidote-(Sr); Tz, tinzenite.



Figure 3. Back-scattered electron image of epidote-(Sr) from the Nagakawara (a) and Hohnomori (b) deposits. The Hohnomori sample reveals the compositional zoning between epidote-(Sr) and piemontite-(Sr). Cal, calcite; Ep-Sr, epidote-(Sr); Pmt-Sr, piemontite-(Sr); Tz, tinzenite.

the ore mineralization, hydrothermal veins penetrate into the ore bodies. The hydrothermal veins mainly consist of an aggregate of rhodochrosite, ganophyllite, taneyamalite, okhotskite, piemontite, tinzenite, and pumpellyite (e.g. Minakawa, 1992; Minakawa 2002). No other Sr-rich minerals except the epidote group minerals were found during this study.

Epidote-(Sr) was found in the Nagakawara and Hohnomori deposits at the Ananai mine. The mineral from the Nagakawara deposit occurs in the form of radial aggregates of acicular-columnar crystals up to 1 cm in length and is scattered in tinzenite veins (Fig. 2). Epidote-(Sr) also occurs as a constituent of the reddish chert and is scattered in the piemontite breccia with calcite at the Hohnomori deposit (Fig. 2), but it is difficult to distinguish piemontite-(Sr) and epidote-(Sr) under a microscope due to their similar optical properties. Figure 3 illustrates the back-scattered electron images of epidote-(Sr) from the Nagakawara and Hohnomori deposits. Epidote-(Sr) from the Nagakawara deposit exhibits no chemical zoning in a single aggregate, while compositional zoning is confirmed in the Hohnomori samples (Fig. 3). Zoning occurs irregularly in a single crystal (Fig. 3b). The bright region in Figure 3b denotes epidote-(Sr), and the dark region denotes piemontite-(Sr), reflecting Fe and Mn contents, respectively. The crystals of epidote-(Sr) of-

 1		1	1 ()	
	Nagal	kawara	Hohno	mori
	wt%	Range**	wt%	Range [†]
SiO_2	34.32	34.21-35.04	34.25	34.00-36.49
Al_2O_3	18.53	15.45-18.61	16.99	13.25-20.09
Fe_2O_3	13.17	12.68-15.11	13.83	9.19-15.28
Mn_2O_3	2.96	1.05-6.05	5.59	1.84-10.42
CaO	11.72	10.86-11.96	12.29	11.93-15.61
SrO	17.63	17.06-18.00	14.57	10.52-16.38
H_2O*	1.71		1.70	
Total	100.04		99.22	
	O = 12.5		O = 12.5	
Si	3.012		3.012	
Al	1.917		1.761	
Fe ³⁺	0.870		0.915	
Mn^{3+}	0.198		0.374	
Ca	1.102		1.158	
Sr	0.897		0.743	
OH*	1		1	
Total	8,996		8,963	

Table 2. Representative chemical compositions of epidote-(Sr) from the Ananai mine

^{*} H_2O was calculated as OH = 1.

** Range of 41 analyses and [†]range of 85 analyses for epidote group minerals.

Table 3. X-ray powder diffraction data for epidote-(Sr) and clinozoisite-(Sr)

			I	Epidote-(S	Sr)	Clinozoisite-(Sr)*					Epidote-(Sr)		Clinozoisite-(Sr)*		
h	k	l	I/I ₀	$d_{\rm obs.}$	$d_{\text{calc.}}$	I/I ₀	d _{obs.}	h	k	l	I/I ₀	d _{obs.}	$d_{\text{calc.}}$	I/I ₀	d _{obs.}
0	0	1	2	9.31	9.32	3	9.29	2	2	1	11	2.14	2.14	24	2.11
1	0	0			8.12	3	8.05	2	2	-3	13	2.11	2.11		
1	0	-1	7	7.96	7.98			0	2	3	21	2.09	2.09	11	2.07
1	0	1	1	5.16	5.16			2	0	3			2.09		
1	0	-2	20	5.04	5.04	23	5.05	4	0	0			2.03	8	2.01
0	1	1	1	4.83	4.83	9	4.78	3	0	-5			1.962	5	1.959
1	1	0	5	4.64	4.64	3	4.59	3	2	0	1	1.958	1.956		
2	0	0	12	4.06	4.06	9	4.02	2	2	2	12	1.901	1.905	16	1.883
2	0	-2	4	3.99	3.99			3	1	2			1.893		
1	1	1	2	3.81	3.81	6	3.76	2	2	-4	9	1.882	1.882	21	1.872
0	1	2	2	3.60	3.60	2	3.56	1	3	0			1.836	1	1.814
2	1	-1	42	3.50	3.50	18	3.48	0	2	4			1.798	2	1.781
1	0	2	5	3.46	3.47	5	3.43	5	0	-2	3	1.781	1.781		
1	0	-3	2	3.42	3.41			0	1	5			1.771	1	1.754
2	1	0	4	3.30	3.30			2	3	-1	3	1.735	1.736	4	1.717
2	0	1	23	3.26	3.26	25	3.22	4	1	-5	6	1.708	1.709	8	1.706
0	0	3	3	3.11	3.11	4	3.09	3	0	-6			1.682	3	1.679
3	0	-1	1	2.96	2.95	1	2.99	1	0	-6	12	1.658	1.658	7	1.648
3	0	-2			2.93			5	1	-1	18	1.650	1.651		
1	1	-3	100	2.92	2.92	100	2.90	1	3	-3			1.649	18	1.632
0	2	0	32	2.83	2.83	48	2.79	4	2	-4	11	1.629	1.630		
0	1	3	41	2.72	2.72	26	2.70	3	2	2			1.637	8	1.618
1	2	0	12	2.67	2.67	18	2.64	4	0	-6			1.593	16	1.592
3	1	-1	42	2.61	2.61	24	2.60	1	1	5	10	1.604	1.604		
2	0	2	49	2.58	2.58	15	2.55	3	3	-1	6	1.591	1.588	3	1.572
1	0	-4	5	2.54	2.54	9	2.52	4	1	2	6	1.567	1.567	9	1.548
1	2	-2	3	2.47	2.47	11	2.44	6	0	-4			1.464	3	1.462
3	1	-3	15	2.41	2.41	21	2.40	5	2	-4	7	1.460	1.460	10	1.453
2	2	-1			2.38	2	2.37	3	2	-6	2	1.445	1.445	5	1.439
2	2	-2	9	2.31	2.31	7	2.29	4	0	3			1.448	3	1.429
4	0	-1	22	2.18	2.18	5	2.16	2	1	5	3	1.431	1.430	3	1.414
4	0	-3	4	2.16	2.16			0	4	0	13	1.412	1.413	22	1.397
]	Epidote-(S	r)						Clin	nozoisite-	(Sr)*	
				a (Å)	8.928(5)							a (Å)	8.890(4))	
				b (Å)	5.652(1)							b (Å)	5.5878(18	3)	
				c (Å)	10.244(5))						c (Å)	10.211(4)	
				β°	114.46(4))						β°	115.12(3)	
				$V(\text{Å}^3)$	470.5(3)							$V(\text{\AA}^3)$	459.3(3))	

* Data from Miyajima et al. (2003).

ten include tinzenite, pumpellyite, ganophyllite, and calcite.

OPTICAL AND PHYSICAL PROPERTIES

Epidote-(Sr) exhibits a translucent pale reddish brown to brown color, reflecting the chemical variations, but most typically it exhibits brown color. It reveals a tinge of red that increases with the Mn content. It exhibits pleochroism—X: pale greenish yellow, and Y and Z: pale reddish brown to brownish pink. Epidote-(Sr) is optically biaxial negative with $\alpha = 1.737(2)$, $\beta = 1.780$ (2), $\gamma = 1.792$ (2), and $2V_{calc} = 62^{\circ}$. Perfect cleavage is observed on {001} and twinning on (100). It has a Mohs' hardness of 6.5, and the calculated density is 3.74 g/cm³.

CHEMICAL PROPERTIES

Chemical analyses were performed with a JEOL JXA5400 at Ehime University, and the ZAF method was used for correction. The analytical conditions were set using an accelerating voltage of 15 kV, and the beam current was 0.4 nA. Live time was set for a period of 120 s. The standard materials silicon metal, corundum, iron metal, Mn_2O_3 , CaF_2 , and SrF_2 were used for the analyses of Si, Al, Fe, Mn, Ca, and Sr, respectively. The proportion of H_2O was calculated on the basis of OH = 1 and O = 12 per formula unit. The representative compositions of epidote–(Sr) from the Nagakawara and Hohnomori deposits are listed in Table 2. The Sr content in epidote–(Sr) is approximately 18 wt% that corresponds to a 90% occupancy in the

count 12000 10000 8000 6000 4000 2000 0 n 30 *70* 10 20 40 50 60 80 <u>9</u>0 100 110 120 2θ/deg

A(2) site. The Sr content in the Nagakawara samples is generally higher than that in the Hohnomori samples. Epidote-(Sr) is characterized by high Fe₂O₃ and low Mn₂O₃ contents, as compared to piemontite-(Sr). The Fe₂O₃ content is approximately up to 14 wt%, indicating approximately 90% occupancy in the M(3) site. The compositional variations in Sr-rich epidote group minerals including epidote-(Sr) are also presented in Table 2. The variation in the Fe₂O₃ and Mn₂O₃ contents in the Hohnomori samples is larger than that in the Nagakawara samples. The representative empirical formula of epidote-(Sr) from the Nagakawara deposit is $(Ca_{1.10}Sr_{0.90})_{\Sigma 2.00}(Al_{1.92}$ Fe³⁺_{0.87}Mn³⁺_{0.20})_{\Su_2.99}Si_{3.01}O₁₂(OH), ideally CaSrAl₂Fe³⁺(Si₂O₇) (SiO₄)(OH). The ideal composition corresponds to that of the Sr-analogue of epidote-(Sr).

X-RAY PROPERTIES

The X-ray powder diffraction data of an epidote-(Sr) sample from the Nagakawara deposit, which was mounted on a silicon non-reflection specimen holder, was collected using a Mac Science MX-Labo diffractometer with CuK α radiation (40 kV, 40 mA, 0.5°-0.5°-0.3mm slit) at the Hokkaido University in a step-scanning mode over a 2 θ range of 8°-100° in increments of 0.02° (10 s/step). The intensity of the X-ray was estimated after monochromatization by pyrolytic graphite. The observed *d*-values and intensities are listed in Table 3. The mineral is monoclinic with a space group of $P2_1/m$, a = 8.928 (5), b = 5.652 (1), c = 10.244 (5) Å, $\beta = 114.46$ (4)°, and V = 470.5 (3) Å³. The crystal structure was refined by the program RIETAN2000 (Izumi and Ikeda, 2000) to refine the site occupancy of the Sr atom at the A(1) and A(2) sites.

Figure 4. Rietveld refinement plot of epidote-(Sr). Rietveld calculation based on the epidote structure model (Dollase, 1971) yielded Rwp = 8.61%, Rp = 6.77%, $R_1 = 2.80\%$, and $R_F = 1.53\%$. The refined site occupancies in A(2) and M(3) sites were 0.86Sr + 0.14Ca atom and 0.78Fe + 0.20Mn + 0.02Al atom, respectively.

The structure model used for Rietveld calculation was constructed on the basis of the epidote structure (Dollase, 1971). The site occupancy of A(1), A(2), M(1), M(2), and M(3) sites were refined. The Mn occupancy at the M(3)site was restricted to less than 0.20 to satisfy the empirical formula. Temperature factors were fixed to the epidote data (Dollase, 1971), and the Si-O distances were restricted to less than 1.67 Å to avoid the distortion of SiO₄ tetrahedra. In the Rietveld calculation, a pseudo-Voigt function was used for the profile function and the preferred orientation was corrected by a March-Dollase function. The Rietveld calculation yielded Rwp = 8.61%, Rp =6.77%, $R_{\rm I} = 2.80\%$, $R_{\rm F} = 1.53\%$, and S = 1.907, and Durbin Watson *d*-statistics (Hill and Flack, 1987) were *d*1 = 0.6246 and d2 = 0.4181 (Fig. 4). The obtained structure parameters and interatomic distances are presented in Tables 4 and 5, respectively. The refined site occupancies confirm that the majority of the Sr atoms occupy the A(2)site, and epidote-(Sr) is a new member of the epidote group.

DISCUSSION

The clinozoisite subgroup minerals are classified according to the cation occupancy in the A(2), M(1), and M(3)sites, and five end-members have been proposed as the possible Sr-analogues in an Al-Fe³⁺-Mn³⁺ system (Table 1). The theoretical compositional variation in epidote-(Sr) is Sr/(Ca + Sr) > 0.5 in the A(2) site and $0.5 < Fe^{3+} < 1.5$ in the *M* sites. The Rietveld refinement confirmed that the A(2) site is occupied by the Sr atoms. The averaged A(2)-O distances (2.747 Å) is larger than that of A(1) site (2.587 Å) support the Sr atom in A(2) site and which is



		X	У	Z	Beq*	Occ.**
A(1)	2e	0.764(1)	0.750	0.156(1)	0.76	0.96Ca + 0.04Sr
A(2)	2e	0.595(1)	0.750	0.422(1)	0.92	0.86(1)Sr + 0.14 Ca
M(1)	2e	0.000	0.000	0.000	0.51	0.90(1)Al + 0.10 Fe
M(2)	2e	0.000	0.000	0.500	0.43	1.00(1)Al
M(3)	2e	0.295(1)	0.250	0.220(1)	0.42	0.02Al + 0.78Fe + 0.20M
Si(1)	2e	0.338(1)	0.750	0.037(1)	0.45	1Si
Si(2)	2e	0.685(1)	0.250	0.274(1)	0.45	1Si
Si(3)	2e	0.174(1)	0.750	0.315(1)	0.45	1Si
O(1)	4f	0.246(1)	0.999(1)	0.043(1)	0.70	10
O(2)	4f	0.292(1)	0.973(1)	0.336(1)	0.70	10
O(3)	4f	0.785(1)	0.013(1)	0.329(1)	0.70	10
O(4)	2e	0.041(1)	0.250	0.117(1)	0.70	10
O(5)	2e	0.045(1)	0.750	0.143(1)	0.70	10
O(6)	2e	0.072(1)	0.750	0.418(1)	0.70	10
O(7)	2e	0.509(1)	0.750	0.176(1)	0.70	10
O(8)	2e	0.532(1)	0.250	0.316(1)	0.70	10
O(9)	2e	0.642(2)	0.250	0.109(1)	0.70	10
O(10)	2e	0.076(1)	0.250	0.425(1)	0.70	10

Table 4. Atomic coordinates, equivalent temperature parameters, and occupancy parameters of epidote-(Sr)

* Temperature parameters are fixed in Rietveld calculation.

^{**} Mn occupancy in M(3) site is restricted less than 0.20 to satisfy the empirical formula.

						()		
A(1)-O(7)	2.367(14)		A(2)-O(7)	2.309(11)				
A(1)-O(3)	2.255(11)	×2	A(2)-O(3)	2.710(10)	$\times 2$			
A(1)-O(5)	2.565(14)		A(2)-O(2)	2.749(9)	$\times 2$			
A(1)-O(1)	2.456(11)	×2	A(2)-O(10)	2.698(11)				
A(1)-O(6)	2.937(12)		A(2)-O(2)	2.780(9)	$\times 2$			
A(1)-O(9)	2.997(5)	×2	A(2)-O(8)	2.994(4)	$\times 2$			
<a(1)-o></a(1)-o>	2.587		<a(2)-o></a(2)-o>	2.747				
M(1)-O(4)	1.788(7)	×2	M(2)-O(10)	1.864(10)	$\times 2$	M(3)-O(8)	1.932(14)	
M(1)-O(1)	2.057(9)	×2	M(2)-O(3)	1.995(8)	×2	M(3)-O(4)	2.070(13)	
M(1)-O(5)	1.951(9)	$\times 2$	M(2)-O(6)	1.887(11)	×2	M(3)-O(2)	1.970(9)	$\times 2$
<m(1)-o></m(1)-o>	1.932		<m(2)-o></m(2)-o>	1.915		M(3)-O(1)	2.201(9)	$\times 2$
						<m(3)-o></m(3)-o>	2.057	
Si(1)-O(7)	1.597(11)		Si(2)-O(8)	1.587(18)		Si(3)-O(2)	1.597(10)	$\times 2$
Si(1)-O(9)	1.580(14)		Si(2)-O(3)	1.580(9)	$\times 2$	Si(3)-O(6)	1.660(18)	
Si(1)-O(1)	1.639(9)	×2	Si(2)-O(9)	1.580(14)		Si(3)-O(5)	1.662(12)	
<si(1)-o></si(1)-o>	1.614		<si(2)-o></si(2)-o>	1.582		<si(3)-o></si(3)-o>	1.629	

Table 5. Interatomic distance (Å) of epidote-(Sr)

same to the *A*-O distances observed in the structure of Piemontite-(Sr) (Miyajima et al.,2003). The average *M*-O distances are *M*(1)-O = 1.932 Å, *M*(2)-O = 1.915 Å, and *M*(3)-O = 2.057 Å. The largest *M*-O distance in the *M*(3) site supports the assumption that Fe atoms exist in the *M*(3) site. Figure 5 illustrates the chemical variation of Al-Fe³⁺-Mn³⁺ cations in the clinozoisite subgroup minerals at the *M* site with Sr/(Ca + Sr) > 0.5 composition at the *A*(2) site.

The samples from the Ananai mine contain a substantial amount of Mn³⁺ ions and are indicated in the epidote-(Sr) and piemontite-(Sr) regions in Figure 5. The samples from the Nagakawara deposits are mainly indicated in the epidote-(Sr) region, while the Hohnomori samples exhibit a relatively wide compositional variation between epidote-(Sr) and piemontite-(Sr) (Fig. 5). The Hohnomori samples are present in the form of breccia, and the blocks with various compositions exist in the mother rock (Fig. 2). Moreover, the single crystals from the Hohnomori deposit exhibit irregular compositional zoning (Fig. 3b). The compositional variation in the Hohnomori sample may be due to the interaction between the retrograde metamorphism and the alteration by hydrothermal activity. Since the zoning in a crystal is irregular, the Mn/Fe ratio in the hydrothermal solution might have changed in a complex manner during the crystal growth.



Figure 5. The Al-Fe³⁺-Mn³⁺ diagram in the clinozoisite subgroup group minerals at the *M* site cations with Sr/(Ca + Sr) > 0.5 composition at the *A*(2) site. Closed and open circles indicate the samples from Nagakawara and Hohnomori deposits, respectively.

The compositional zoning in a single crystal of the Nagakawara sample is not distinct, but the compositional difference among the aggregates is remarkable. Epidote-(Sr) from the Nagakawara deposit occurs in the form of radial aggregates in the tinzenite vein, and thus epidote-(Sr) may be formed from the residual hydrothermal fluid after the crystallization of tinzenite. Therefore, the compositional variations in the Nagakawara sample may have been caused by the difference in the residual hydrothermal composition.

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