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Dissakisite-(Ce), a new member of the epidote group and the Mg analogue of allanite-(Ce), from Antarctica

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ABSTRACT

Dissakisite-(Ce), ideally $Ca(Ce,La)MgAl_2Si_3O_{12}(OH)$, occurs in marble on Balchen Mountain, East Antarctica, (72°S, 27°30′E) in association with calcite, dolomite, forsterite, clinohumite, phlogopite, chlorite, ilmenite-geikielite solid solution, spinel, zircon, pyrrhotite, a rare-earth silicate, and a calcium zirconium titanium oxide. Electron microprobe analyses of the more magnesian grain (core) gave SiO_2 32.09, TiO_2 0.89, Al_2O_3 17.67, FeO 1.80, MgO 6.84, CaO 10.75, CdO 0.10, La_2O_3 9.80, Ce_2O_3 16.94, Pr_2O_3 0.86, Nd_2O_3 2.08, Sm_2O_3 0.13, Eu_2O_3 and Gd_2O_3 <0.10, ThO_2 0.08, Y_2O_3 0.04, P_2O_5 0.02, F 0.21, H_2O (calc) 1.54, total 101.75 wt% (corrected for O = F), yielding a formula of $Ca_{1.05}(Ce_{0.57}La_{0.33}Nd_{0.07}Pr_{0.03})Mg_{0.93}Fe_{0.14}Ti_{0.06}Al_{1.91}Si_{2.94}O_{12}(OH)_{0.94}F_{0.06}$. Dissakisite-(Ce) forms anhedral grains 0.05–0.6 mm in diameter. It is pale yellow-brown in thin section and weakly pleochroic with X = pale brown; $Y = Z$ = light yellow-brown, and absorption $X < Y = Z$. Optically, it is biaxial (+), $\alpha = 1.735(3)$, $\beta = 1.741(3)$, $\gamma = 1.758(3)$, $2V_{Z,\ (meas)} = 64.2(3)°$, $2V_{Z,\ (calc)} = 62°$. Dispersion $r < v$, medium. $Y \parallel b$, $Z \wedge a = 23.7°$ (in obtuse angle β). It is monoclinic, space group $P2_1/m$, $a = 8.916(20)$, $b = 5.700(8)$, $c = 10.140(25)$ Å, $\beta = 114.72(14)°$, $V = 468.10$ Å^3, and $Z = 2$. $D_{meas} = 3.75$ (15) g/cm^3, $D_{calc} = 3.97–4.02$ g/cm^3. The most intense X-ray powder diffraction lines are [d (Å) (I)(hkl)]: 9.1(40)(001), 3.50(50)($21\bar{1}$), 2.910(90)($30\bar{2}$,$11\bar{3}$), 2.842(50)(020), 2.698(100)(013,300,120), 2.622(60)($31\bar{1}$), 2.177(40)($12\bar{3}$,$40\bar{1}$), 2.137(40)(221,014), 1.636(40).

Dissakisite-(Ce) is inferred to have formed at about 600 °C as a result of amphibolite-facies metamorphism superimposed on a regional granulite-facies terrain, for which the estimated P-T conditions are ≥7 kbar, 700–750 °C. The name is derived from the Greek, dissákis (δισσάκις), meaning "twice over," for a Mg analogue of allanite having been described twice.

INTRODUCTION

The mineral is the Mg analogue of allanite-(Ce) with an ideal formula $CaCeMgAl_2Si_3O_{12}(OH)$. Geijer (1927) originally described a mineral he considered to be the Mg analogue of allanite, which he named "magnesium orthite." However, his analysis gave a formula closer to $CaCeMg_2AlSi_3O_{11}(OH)F$. Peacor and Dunn (1988) reexamined material from the type locality of "magnesium orthite" (Östanmossa mine, Norberg district, Sweden), obtained a similar formula to Geijer's, and renamed it dollaseite-(Ce) because orthite is no longer an acceptable term for allanite and because dollaseite-(Ce) is not the Mg analogue of allanite (= orthite). Geijer (1927) also reported "orthite" with a formula $CaREE_{0.97}(Mg_{1.08}Fe^{2+}_{0.43}Mn_{0.02})(Al_{1.16}Fe^{3+}_{0.43})Si_{3.10}O_{11.57}(OH)_{1.16}F_{0.27}$, that is, a composition intermediate among what is now designated as allanite-(Ce), dollaseite-(Ce), and a Mg analogue of allanite-(Ce), one in which Mg > Fe^{2+}. Enami and Zang's (1988) most magnesian allanite, $Ca_{1.07}REE_{0.95}Mg_{0.84}Fe_{0.09}Al_{2.03}Si_{3.00}O_{12}(OH)$, closely approaches the Mg analogue of allanite in composition. Meyer (1911), Hanson and Pearce (1941), Kimura and Nagashima (1951), Khvostova and Bykova (1961), Kalinin et al. (1968), and Treloar and Charnley (1987) reported analyses of allanite with X_{Mg} = Mg/(Fe^{2+} + Mg) = 0.50–0.85. Moëlo et al. (1974) reported an allanite with the formula $CaCeMgAl_2Si_3O_{12}(OH)$ but gave no analytical data on the Fe/Mg ratio. We propose the name dissakisite-(Ce) for the Mg analogue of

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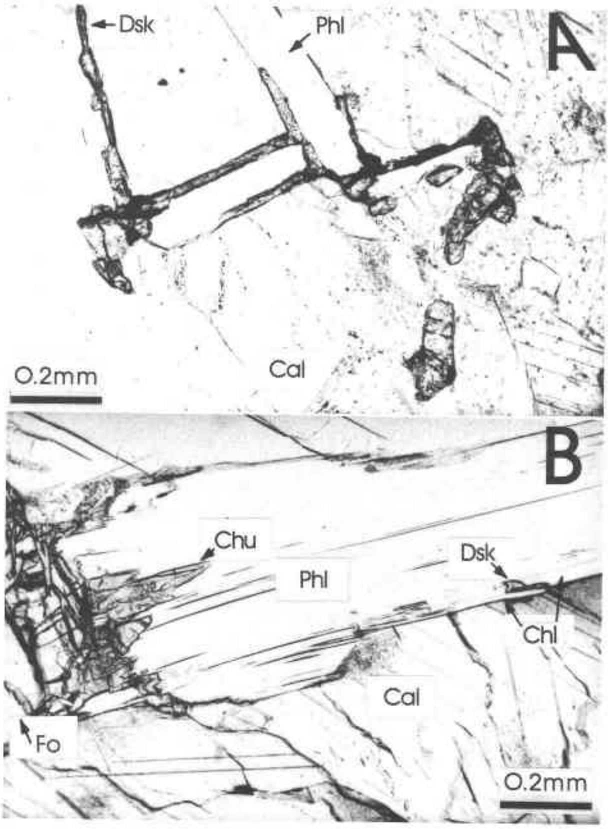

Fig. 1. Photomicrographs of marble, sample EG88011814, Balchen Mountain, Antarctica. Plane light. (**A**) Selvages and grains of dissakisite-(Ce) (Dsk) around phlogopite (Phl) and in calcite (Cal). (**B**) Dissakisite-(Ce) between chlorite (Chl) and phlogopite near clinohumite (Chu) formed from forsterite (Fo).

allanite and describe a specimen from Antarctica. This name is derived from the Greek, dissákis (δισσάκις), an adverb meaning "twice over," in reference to the Mg equivalent of allanite having been described twice. It is pronounced dis-sá-kis-ite. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names of the IMA. The type material is deposited in the Smithsonian Institution as specimen no. NMNH 168421.

OCCURRENCE

Dissakisite-(Ce) occurs in a single sample of marble (no. EG88011814) from 72°S, 27°30′E on Balchen Mountain in the eastern Sør Rondane Mountains, Antarctica (Asami et al., 1989; Grew et al., 1989). In hand specimen, the marble is light gray, medium-grained, with conspicuous forsterite and phlogopite. In thin section, the dominant minerals are calcite (maximum Mg: $Ca_{0.91}Mg_{0.09}CO_3$), forsterite ($Mg_{1.98}Fe_{0.07}Si_{0.98}O_4$), phlogopite [$(K_{1.77}Na_{0.07})(Mg_{5.55}Fe_{0.13}Al_{0.30}Ti_{0.09})(Al_{2.47}Si_{5.53})O_{22}(OH)_{3.34}F_{0.66}$], and spinel ($Mg_{0.92}Fe_{0.07}Zn_{0.01}Al_2O_4$), and minor minerals are clinohumite [variable in Ti, one analysis is $Mg_{8.72}Mn_{0.01}Fe_{0.25}Ti_{0.21}Si_{3.90}O_{16.43}(OH)_{1.13}F_{0.44}$], chlorite ($(Ca_{0.01}Mg_{9.32}Fe_{0.18}Al_{2.40}Ti_{0.01})(Al_{2.28}Si_{5.72})O_{20}(OH)_{16}$], dolomite [$Ca_{1.05}Mg_{0.94}Fe_{0.01}(CO_3)_2$], pyrrhotite, ilmenite-geikielite solid solution (maximum Mg: $Mg_{0.55}Fe_{0.43}TiO_3$), dissakisite-(Ce) (Fig. 1, Table 1), zircon, and apatite (Table 2) (chemical data from Grew et al., 1989, and unpublished data except analyses in Tables 1 and 2 and analyses of calcite and F content in phlogopite and clinohumite, which were obtained by E. J. Essene). The pyrrhotite contains lamellae of pent-

TABLE 1. Analyses of dissakisite-(Ce)

	1	2a	2b	3	4
			Oxide wt%		
SiO_2	31.73	32.09	32.19	31.85	31.60
TiO_2	0.89	0.89	1.22	0.02	0.20
Al_2O_3	17.02	17.67	17.78	10.09	19.00
Fe_2O_3	—	—	—	5.83	2.37
FeO	1.96*	1.80*	2.04*	5.34	4.26
MnO	0.03	0	0.02	0.27	0.09
MgO	6.73	6.84	6.71	7.42	4.00
CaO	10.64	10.75	11.00	9.57	12.80
CdO	0.11	0.10	0.08	—	—
La_2O_3	9.92	9.80	9.58	15.50**	22.48†
Ce_2O_3	17.64	16.94	17.01	11.66	
Pr_2O_3	0.93	0.86	0.83		
Nd_2O_3	2.44	2.08	2.25		
Sm_2O_3	0.13	0.13	0.10		
Eu_2O_3	<0.10	<0.10	<0.10		
Gd_2O_3	<0.10	<0.10	<0.10		
Dy_2O_3	<0.05	<0.05	<0.05		
Er_2O_3	<0.05	<0.05	<0.05		
ThO_2	0.09	0.08	0.04	—	1.32
Y_2O_3	0.03	0.04	0.02	—	—
P_2O_5	0.02	0.02	0.04	—	—
F	0.27	0.21	0.18	0.87	—
H_2O (meas)	—	—	—	1.79	1.87
H_2O (calc)	1.49‡	1.54‡	1.57‡	—	—
−O = F	−0.11	−0.09	−0.08	−0.37	—
Total	101.96	101.75	102.58	99.84	99.99
			Formulae		
	12 O + (OH, F)			13 (O, OH, F)	
Si	2.93	2.94	2.92	3.10	2.89
Ti	0.06	0.06	0.08	0.00	0.01
Al	1.85	1.91	1.90	1.16	2.05
Fe^{3+}	—	—	—	0.43	0.16
Fe^{2+}	0.15	0.14	0.15	0.43	0.33
Mn	0.00	0.00	0.00	0.02	0.01
Mg	0.93	0.93	0.91	1.08	0.54
Ca	1.05	1.05	1.07	1.00	1.25
La	0.34	0.33	0.32	0.55**	
Ce	0.60	0.57	0.57	0.42	
Pr	0.03	0.03	0.03		
Nd	0.08	0.07	0.07		
Th	0	0	0	—	0.03
Sum REE	1.05	1.00	0.99	0.97**	0.75†
Sum Cat	8.02	8.03	8.02	8.19	8.02
F	0.08	0.06	0.05	0.27	—
OH	0.92‡	0.94‡	0.95‡	1.16	1.14

Note: Explanation of numbers is as follows. 1 and 2: Dissakisite-(Ce), two grains, Sør Rondane Mountains, Antarctica (sample no. EG88011814), electron microprobe analysis, this study. For 2, a = core, b = rim. 3: Subaluminous ferroan dissakisite-(Ce), Östanmossa, Sweden, wet chemical analysis, Geijer (1927). 4: Ferroan dissakisite, Fedorovskoye deposit, Southern Yakutia, USSR, wet chemical analysis, Khvostova and Bykova (1961).

* All Fe assumed to Fe^{2+}.

** Given as $(La,Nd,Pr)_2O_3$ etc. Sum REE was calculated assuming a molecular weight of 331, Geijer (1927).

† Given as REE_2O_3. Formula calculated assuming a molecular weight of 328.

‡ Calculated assuming 12 O + (OH, F).

TABLE 2. Analyses of apatite and rare-earth-element silicate from Antarctica (sample no. EG88011814)

	Oxide wt%			Formulae	
	Apatite	REE silicate		Apatite	REE silicate
SiO_2	0.20	18.60	Si	0.02	3.79
TiO_2	0.05	13.35	Ti	0	2.05
Al_2O_3	0.02	4.22	Al	0	1.01
FeO	0.05	3.75	Fe	0	0.64
MnO	0.03	0.02	Mn	0	0
MgO	0.03	3.26	Mg	0	0.98
CaO	53.83	2.66	Ca	5.03	0.58
P_2O_5	39.95	0.09	P	2.95	0.02
La_2O_3	0.17	17.53	La	0.01	1.32
Ce_2O_3	0.33	32.94	Ce	0.01	2.45
Pr_2O_3	0	2.09	Pr	0	0.15
Nd_2O_3	0.08	5.17	Nd	0	0.38
Sm_2O_3	0	0.63	Sm	0	0.05
ThO_2	0.05	0.24	Th	0	0.01
F	2.70	0.27	F	0.75	0.17
H_2O*	0.44	—	OH	0.25	—
O = F	−1.14	−0.11	sum REE	0.02	4.36
Sum	96.79**	104.71	cation sum	8.02	13.43

Note: All Fe as FeO. Apatite formula normalized to 12 O + (F, OH). REE silicate formula normalized to 22 O.

* Weight percent calculated from formula.

** Cl content is estimated to be no more than a few tenths weight percent, as no Cl was detected in element scan.

landite and is associated with tiny granules of chalcopyrite. A quantitative energy-dispersive analysis of one pentlandite lamella gave Fe 32, Co 5, Ni 30, S 33, total 100 wt% (M. G. Yates, personal communication; there was possibly some interference from the pyrrhotite host). A rare earth silicate similar to chevkinite (Table 2) and a calcium zirconium titanium oxide, probably zirconolite, were identified using backscattered electron (BSE) images and energy dispersive X-ray (EDX) analyses. The zirconolite occurs as small inclusions in geikielite and as rims on zircon. The EDX analyses of the zirconolite reveal significant amounts of Fe, Th, and U in addition to Ca, Ti, and Zr.

Forsterite grains are largely fresh; a few serpentine seams cut the grains. In addition, forsterite is locally embayed by aggregates of colorless chlorite and yellow clinohumite. Chlorite also replaces pale green spinel and pale brown phlogopite. Calcite constitutes most of the matrix. Dolomite is common as exsolution lamellae in calcite, but a few discrete carbonate grains were found by microprobe analysis and BSE images to be dolomite. Dissakisite-(Ce) occurs sparingly in thin section as a few anhedral grains 0.05–0.6 mm in diameter. For example, it occurs (1) in calcite between forsterite grains, (2) in dolomite adjacent to forsterite, (3) as selvages between phlogopite and carbonate (Fig. 1A), (4) with chlorite formed from phlogopite (Fig. 1B), and (5) intergrown with geikielite.

In a second sample of marble from the same locality (no. MA88011831), a mineral provisionally identified as dissakisite-(Ce) also occurs between forsterite and phlogopite.

The ferromagnesian minerals in the marble are highly magnesian. The Mg-Fe partitioning increases as follows: geikielite < dissakisite < spinel < forsterite < clinohumite < calcite, phlogopite < chlorite < dolomite (Grew et al., 1989), consistent with sequences reported elsewhere (Albee, 1968; Windley et al., 1989). The F-OH partitioning increases as follows: dissakisite < phlogopite < clinohumite.

The eastern Sør Rondane Mountains are a high-grade polymetamorphic terrane. Asami et al. (1989) and Grew et al. (1989) inferred (1) an early high-grade event attaining the granulite facies in the Balchen Mountain area (T = 700–750 °C, $P \geq 7$ kbar) on a clockwise prograde path passing through the kyanite stability field, (2) a subsequent amphibolite-facies event associated with migmatization at 500–600 °C, and (3) retrogression in the greenschist facies. Asami et al. (1990) and Makimoto et al. (1990) estimated temperatures of 520–700 °C from garnet rims and biotite at two localities on Balchen Mountain within 5 km of the dissakisite-(Ce) loacality. These temperature values are attributed to the amphibolite-facies event.

The assemblage forsterite + spinel + magnesian calcite + phlogopite + geikielite in sample EG88011814 is attributed to the granulite-facies event. With influx of REE-bearing, mineralizing aqueous fluids during the amphibolite-facies event, the high-grade assemblage was partly replaced by chlorite + clinohumite and locally with dissakisite-(Ce); dolomite exsolved from magnesian calcite. The zirconolite rims on zircon may have formed at this time by a reaction such as the following: zircon + calcite + geikielite + mineralizing aqueous fluid = clinohumite + zirconolite + CO_2. Grew et al. (1989) also inferred that introduced REE resulted in allanite selvages between calcite and scapolite on Austhamaren, an exposure 40 km northwest of the Balchen Mountain locality. Dissakisite-(Ce) formed at temperatures near 600 °C during the amphibolite-facies event. This estimate is based not only on the temperatures cited above but also on a temperature of 650 °C calculated from the most magnesian calcite (8.8 mol% magnesite) associated with dissakisite-(Ce) and using the calcite-dolomite solvus of Anovitz and Essene (1987). No data are available to constrain the pressure for dissakisite-(Ce); most likely, pressure could have approached the 7 kbar estimated for the early event.

PHYSICAL AND OPTICAL PROPERTIES

Dissakisite-(Ce) forms anhedral grains 0.05–0.6 mm in diameter. It is pale yellow-brown in thin section of 0.03 mm thickness and weakly pleochroic with X = pale brown, $Y = Z$ = light yellow-brown, and absorption $X < Y = Z$. The streak is presumed to be white; the luster is vitreous and transparent. No cathodoluminescence was observed in the electron beam of the microprobe. The density measured using heavy liquids is 3.75(15) g/cm³ (P. J. Dunn, personal communication); the calculated density is 3.97–4.02 g/cm³. No cleavage was observed, but by analogy to other members of the epidote group, there is probably a {001} cleavage.

Optically, dissakisite-(Ce) is biaxial positive, with

$2V_{Z,\,(meas)} = 64.2(3)°$, $2V_{Z,\,(calc)} = 62°$ and $\alpha = 1.735(3)$, $\beta = 1.741(3)$, $\gamma = 1.758(3)$ (white light). Dispersion is $r < v$, medium. The optical orientation is $Y \parallel b$, $Z \wedge a = 23.7°$ (in the obtuse angle β; this is less than the values of 26–67° reported for allanite, Deer et al., 1986). Calculation of the Gladstone-Dale relationship for the three analyses and D_{meas} of dissakisite-(Ce) yields a compatibility index of −0.030 to −0.040, that is, in the good to excellent categories (Mandarino, 1981).

X-RAY CRISTALLOGRAPHY

Weissenberg and precession photographs show that dissakisite-(Ce) has space group $P2_1/m$ or $P2_1$. By analogy with members of the epidote group, $P2_1/m$ is presumed to be the correct space group. Lattice parameters were refined from the X-ray powder diffraction data obtained using a 114.6 mm Gandolfi camera, Cu$K\alpha$ radiation and Si internal standard (Table 3): $a = 8.916(20)$, $b = 5.700(8)$, $c = 10.140(25)$ Å, $\beta = 114.72(14)°$, $V = 468.10$ Å^3, $Z = 2$.

TABLE 3. Powder X-ray diffraction data for dissakisite-(Ce) from Antarctica (sample no. EG88011814)

I_{obs}*	d_{obs} (Å)	d_{calc} (Å)**	*hkl*	I_{obs}*	d_{obs} (Å)
40	9.1	9.2	001†	20	1.879
20	8.1	8.1	100†	5	1.846
5	5.12	5.11	101†	2	1.820
2	4.85	4.85	011†	5	1.782
10	4.59	4.63	$11\bar{1}$	5	1.750
		4.61	002†	5	1.698
5	3.77	3.76	$11\bar{2}$†	2	1.689
50	3.50	3.51	$21\bar{1}$†	30	1.651
30	3.25	3.26	$21\bar{2}$	40	1.636
		3.24	201	30	1.590
90	2.910	2.922	$30\bar{2}$	30	1.560
		2.905	$11\bar{3}$†	10	1.531
50	2.842	2.850	020†	5	1.460
100	2.698	2.703	013	20	1.423
		2.700	300	2	1.412
		2.688	120†	5	1.379
60	2.622	2.616	$31\bar{1}$†	10	1.298
20	2.559	2.557	202†	10	1.280
10	2.495	2.508	$10\bar{4}$	5	1.258
		2.501	$20\bar{4}$	5	1.194
		2.490	121	5	1.158
10	2.398	2.403	$31\bar{3}$†		
		2.401	$22\bar{1}$		
20	2.368 (BR)	2.340	301		
		2.333	212		
		2.331	220		
40	2.177	2.178	$12\bar{3}$		
		2.177	$40\bar{1}$		
40	2.137	2.140	221†		
		2.135	014		
5	2.120	2.122	$31\bar{4}$		
		2.118	$22\bar{3}$†		
5	2.081	2.089	023		
		2.075	$41\bar{2}$		
2	2.070	2.066	203		
2	2.032	2.034	$41\bar{1}$		
		2.026	$20\bar{5}$		
		2.025	400		

* Intensities visually estimated utilizing a Gandolfi photograph obtained with 114.6-mm camera diameter, Cu$K\alpha$ radiation, and Si as an internal standard.

** The *d*-values are calculated from refined unit-cell parameters $a = 8.916(20)$, $b = 5.700(8)$, $c = 10.140(25)$ Å, $\beta = 114.72(14)°$.

† Reflection used in least-squares refinement of lattice parameters. Where two or more d_{calc} match a single d_{obs}, indices were chosen as for dollaseite-(Ce) (Peacor and Dunn, 1988), for which single-crystal intensities were used to resolve ambiguities in indices.

CHEMICAL COMPOSITION

Dissakisite-(Ce) from Antarctica

Dissakisite-(Ce) was analysed using the Cameca Camebax wavelength dispersive electron microprobe at the University of Michigan. Operating conditions were 15 kV, sample current 10 nA, and data were reduced with the Cameca version of the PAP correction program. Standards are as follows: zoisite (Si, Al, Ca$K\alpha$), $MgTiO_3$ (Ti$K\alpha$), Simmons thorianite (Th$M\alpha$), $Y_3Al_5O_{12}$ (Y$L\alpha$), $LaNbO_4$ (La$L\alpha$), $CeWO_4$ (Ce$L\alpha$), Drake-Weill glass (Pr$L\beta$), $Sm_3Ga_5O_{12}$ (Sm$L\alpha$), $Eu_3Ga_5O_{12}$ (Eu$L\beta$), $Gd_3Ga_5O_{12}$ (Gd$L\beta$), $Dy_3Ga_5O_{12}$ (Dy$L\alpha$), $Er_3Ga_5O_{12}$ (Er$L\beta$), Kakanui hornblende (Fe, Mg, Na$K\alpha$), CdS (Cd$L\alpha$), topaz (F$K\alpha$), and Broken Hill rhodonite (Mn$K\alpha$). The rare earth element (REE) analyses do not have significant peak overlaps; $L\beta$ peaks were used to avoid interferences for Pr, Eu, Gd, and Er. Roeder's (1985) analytical procedure did not appear to be appropriate for the Cameca microprobe used in this study.

The REE standards chosen in this study are preferable to the Drake-Weill glasses because they have higher concentrations of REE, comparable to those of La and Ce in dissakisite-(Ce). Even for the other REE, the Drake-Weill glasses (which are widely used for allanite analyses) are not convenient as REE standards because the count rates are too low for precise results with routine choices of current, voltage, and counting times. Estimates of errors are 2–4% for major elements and 10% of the amount present for the minor elements. Analyses of the Drake-Weill glasses as unknowns gave REE values within 10% of the reported value for all the REE analyzed. Counting times of 200 s were used to improve counting statistics for F and Pr; all other elements were determined using a total of 40000 counts (0.5% 2σ) or 30 s, whichever came first. Detection limits of the minor elements are 0.05 wt%. To avoid serious background interferences for the transition metal and rare earth elements, a background was determined where no interference exists and a slope based on a wavelength scan for the unknown was applied. For the standards, backgrounds were measured in the usual way.

The analytical totals are high, which suggests that there is a small systematic error in the REE analyses, and consequently the calculated densities of 3.97–4.02 gm/cm^3 are substantially higher than the measured density of 3.75 g/cm^3. An underestimate of D_{meas} resulting from the small grain size and contamination with phlogopite could also have contributed to this discrepancy.

Differences among the three analyses of two grains (core and rim on one) suggest small variations in Mg ($X_{Mg} = 0.854$–0.871), Al, and Ti, but the differences are within the precision of the measurements as indicated by counting statistics for 2σ uncertainties. Fifteen analyses of four grains (1–6 analyses per grain) at the National Institute of Polar Research (NIPR) (Grew et al., 1989) also show no significant compositional variation from grain to grain within analytical uncertainty. In addition, values for MnO, Cr_2O_3, and ZnO (all ≤ 0.15 wt%) measured at NIPR are interpreted to be not significant.

Recalculation of the analyses by normalizing to 12 O + (OH,F) yields empirical formulae close to an ideal dissakisite formula $Ca(Ce,La)MgAl_2Si_3O_{12}(OH)$ (Table 1). Adopting the Levinson rules for the naming of REE minerals (Levinson, 1966), the name is suffixed to reflect the dominant REE: dissakisite-(Ce).

Solid solutions in dissakisite and allanite

Dissakisite-(Ce) from Antarctica (this study) and China (Enami and Zang, 1988) closely approaches the ideal formula $Ca(Ce,La)MgAl_2Si_3O_{12}(OH)$; the major deviation, aside from the other REE, is minor Ti in the dissakisite-(Ce) from Antarctica. Several other allanite samples reported to have $Mg > Fe^{2+}$ have compositions in reasonable accord with a theoretical dissakisite-(Ce)–allanite-(Ce) solid solution, $Ca(Ce,La)(Mg,Fe^{2+})Al_2Si_3O_{12}(OH)$. The "orthite" studied by Geijer (1927) (analysis reproduced in Table 1) is a subaluminous ferroan dissakisite intermediate in composition between dissakisite-allanite on the one hand and dollaseite on the other, allowing for $Fe^{3+} = Al$ exchange. Its SiO_2 content of 31.85 wt% is characteristic of allanite (Hasegawa, 1960; Khvostova, 1962), and its stoichiometry fits the epidote group formulation in that $Mg + Fe^{2+} + Fe^{3+} + Al = 3.10$ and $Ca + REE = 1.97$. The two analyses reported by Khvostova and Bykova (1961) also give formulae in reasonable accord with allanite and dissakisite (the more magnesian is listed in Table 1). Treloar and Charnley's (1987) "chromian allanite" is chromian dissakisite-(Ce) and dissakisite-(La). The most magnesian reported has the following formula: $Ca_{1.06}REE_{0.87}Mg_{0.64}Fe_{0.11}Cr_{0.29}Al_{1.95}Si_3O_{12}(OH)$. Of the remaining allanites reported to be magnesian, Meyer's (1911) scandian allanite and the allanite of Kalinin et al. (1968, Table 2, no. 14) are deficient in A-site cations ($REE + Ca + Th + Sr + Mn = 1.6–1.7$ per 3 Si) and thus deviate somewhat from the ideal allanite-dissakisite formulation. In addition, Meyer (1911) reported 7.34 wt% H_2O. The allanite studied by Hanson and Pearce (1941) deviates markedly from this formulation, and Hasegawa (1960, p. 351) thought this specimen "should be subjected to re-examination." The analysis of Hanson and Pearce (1941) differs from that of Goddard and Glass (1940) for allanite from the same locality, which contains 1.44 wt% MgO ($X_{Mg} = 0.20$). Kimura and Nagashima's (1951) allanite (cited in Hasegawa, 1960) is unusual in its high BeO (1.35 wt%) and total yttrium oxides, which are reported as $[Y]_2O_3 = 9.75$ wt%.

Allanite is complex in compositional substitutions. The most important substitutions are the following: (1) REE, Th, Mn, and Sr for Ca on the A site; (2) Be and Ge for Si on the tetrahedral sites; (3) Ti, Mn, Cr, Fe^{2+}, Mg, and Ga for Fe^{3+} and Al on the M sites, and (4) F and OH for O on the anion sites (Hasegawa, 1960; Khvostova, 1962; Johan et al., 1983; Deer et al., 1986; Treloar and Charnley, 1987; Burt, 1989). Heterovalent substitutions on the A and M sites are coupled, e.g., $REE + (Fe^{2+}, Mg) = Ca + (Al, Fe^{3+})$ or solid solution toward clinozoisite and epidote, and $Th + 2(Fe^{2+}, Mg) = Ca + 2(Al, Fe^{3+})$. In relating dissakisite-(Ce) to other allanite-group minerals, we will consider variations involving Mg, Fe^{2+}, Fe^{3+}, and Al. We will consider only Mn-poor allanites because of the possibility of substitutions such as Mn = Ca (Hasegawa, 1960), $Mn = (Fe^{2+}, Mg)$, and $Mn^{3+} = (Al, Fe^{3+})$ (see also Deer et al., 1986).

Figure 2 relates clinozoisite-epidote (Czo, Ep), allanite (Aln), and dissakisite (Dsk) as three end-members in terms of M-site compositions. In most cases, composition of the M site is consistent with A site composition; that is, the M-site compositions plot in the same field as that determined by the proportion of rare earths in the A site $[X_{(Aln+Dsk)} = REE/(REE + Ca - 1)]$. The data on M-site composition are also consistent with complete miscibility between epidote-clinozoisite and allanite deduced from occupancy of the A site (e.g., Deer et al., 1986; Pan and Fleet, 1990). This miscibility extends to Mg-bearing compositions, implying a certain extent of ternary solid solution. However, the absence of compositions along the clinozoisite–epidote-dissakisite join (except near the respective end-members) suggests that solid solution in Fe-poor compositions may be limited. Ca contents also suggest such a limitation. The $Ca/(Fe + Mg + Ca)$ ratio in dissakisite from the Sør Rondane Mountains and China does not deviate significantly from 0.5, whereas in allanite and ferroan dissakisite, $Ca/(Fe^{2+} + Mg + Ca)$ typically ranges from 0.5 to 0.6.

However, not all the variation in $(Al + Fe^{3+})$ can be attributed to the substitution $REE + (Fe^{2+}, Mg) = Ca + (Al, Fe^{3+})$. Figure 3 is a plot of allanite and dissakisite containing little epidote-clinozoisite in solid solution, that is, $Ca \leq 1.3$ per 3 Si. Nonetheless, $R^{3+} = Al + Fe^{3+}$ is inversely correlated with $R^{2+} = Fe^{2+} + Mg + Mn$, and the slope of a least-squares fit to the data (excluding subaluminous ferroan dissakisite and dollaseite) is close to -1. For the same set of 73 analyses, R^{3+} is not correlated with Ca: $Ca + 0.87 + 0.11R^{3+}$ (Correlation coefficient = 0.065 vs. 0.33 for the data plotted in Fig. 3). The inverse correlation illustrated in Figure 3 is better explained by exchanges not involving Ca and REE, such as $(Fe^{2+}, Mg) + (OH) = (Al, Fe^{3+}) + O$, which leads to an oxyallanite end-member, $CaREE(Al,Fe^{3+})_3Si_3O_{13}$. Khvostova (1962) reported that almost no H_2O is released from allanite heated to high temperature (most H_2O is released at 160–200 °C) and concluded that OH is absent in unaltered allanite. Consequently, oxyallanite should be considered as a potential component of allanite, but given the altered state of most allanite and the scatter in Figure 3, its presence will be hard to demonstrate.

In the magnesian allanite minerals, F could be an important factor in determining compositions along the dissakisite-dollaseite join through the $Al + O = Mg + F$ substitution proposed by Peacor and Dunn (1988). For

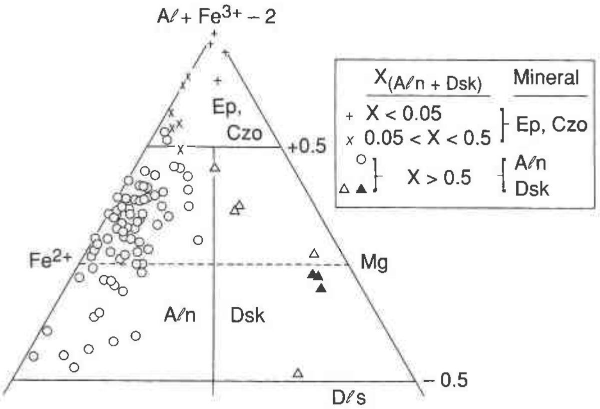

Fig. 2. Plot of 99 allanite, dissakisite, clinozoisite, and epidote compositions with known REE contents in terms of M site occupancy: Al + Fe^{3+} − 2, Fe^{2+}, and Mg. The analyses have been normalized to 3 Si instead of 13(O,OH,F) or 12.5 O (excluding H_2O and F) because in many of the older wet chemical analyses, only total REE are reported. Sources: Hasegawa (1960), Deer et al. (1986, Tables 4 and 7), Khvostova and Bykova (1961), Khvostova (1962), Frondel (1964), Kalinin et al. (1968), Popova et al. (1980), Ivanov et al. (1981), Enami and Zang (1988), Keith et al. (1968), Lee et al. (1966), and this study (filled symbols). Criteria for selection of analyses include CaO ≥ 9.1 wt%, 30 < SiO_2 < 34 wt% (higher SiO_2 accepted for CaO > 11 wt%), MnO ≤ 1.2 wt%, H_2O^+ < 3 wt%, $Na_2O + K_2O \leq 1\%$, $ThO_2 \leq 4\%$, $TiO_2 \leq 2\%$, minimal contents of other constituents, and availability of Fe^{2+} and Fe^{3+} analyses (except for magnesian dissakisite, in which Fe is assumed to be Fe^{2+}, and for one epidote, for which Khvostova, 1962, Table 11, did not report FeO). Solid lines are the boundaries for the fields of clinozoisite-epidote (Al + Fe^{3+} > 2.5, Czo-Ep), allanite (Fe^{2+} > Mg, Aln), dissakisite (Mg > Fe^{2+}, Dsk), and dollaseite (Mg > Fe^{2+}, Al + Fe^{3+} < 1.5, Dls). The horizontal line dividing the field for Czo, Ep from the fields for Aln and Dsk is based on the connection between the occupancies of the M and A sites through the coupled substitution Ca + (Al, Fe^{3+}) = REE + (Fe^{2+}, Mg). Symbols are based on $X_{(Aln+Dsk)}$ = REE/(REE + Ca − 1) with Y added to REE and Sr added to Ca.

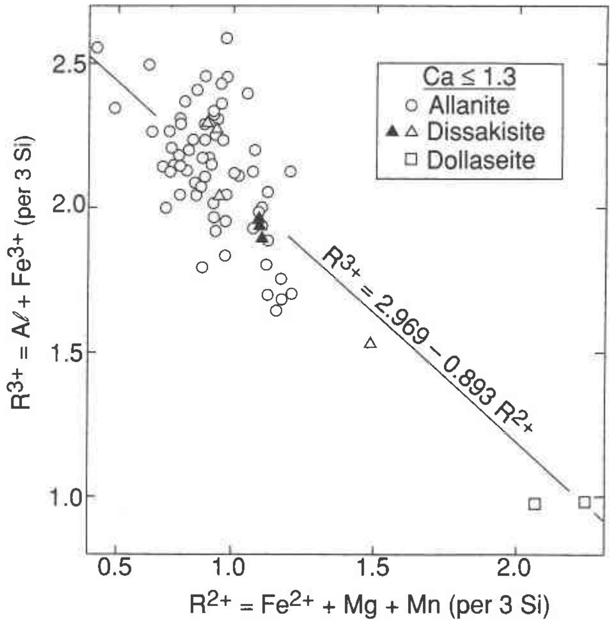

Fig. 3. Compositions of allanite-(Ce), dissakisite-(Ce), and dollaseite-(Ce) in terms of R^{3+} = Al + Fe^{3+} and R^{2+} = Mg + Fe^{2+} + Mn normalized to 3 Si (see Fig. 2). Data include 74 allanite and dissakisite analyses plotted in Figure 2 (filled symbols, this study) for which Ca ≤ 1.3 ions per 3 Si and two dollaseite analyses from Geijer (1927) and Peacor and Dunn (1988). Line is least-squares fit of the 73 analyses for which R^{2+} < 1.3, correlation coefficient R = 0.330 (for all 76 analyses, $R^{3+} = 3.010 - 0.938\ R^{2+}$, R = 0.640).

example, F contents of dissakisite and dollaseite increase with increasing F in the associated humite-group mineral, as determined by species: 0.18–0.27 wt% F in dissakisite with clinohumite (this study), 0.87 wt% F in subaluminous ferroan dissakisite (Table 1) with chondrodite (Geijer, 1927), and 3.0–3.31 wt% F in dollaseite-(Ce) with norbergite (Geijer, 1927; Peacor and Dunn, 1988).

PETROGENESIS

Dissakisite-(Ce) has been found in a variety of parageneses. The subaluminous, ferroan dissakisite-(Ce) at Östanmossa, Sweden, occurs in tremolite skarn with calcite and locally with chondrodite as well as in magnetite ore, associated with cerite and actinolite skarn (Geijer, 1927). Fe-poor dollaseite-(Ce) occurs at the same locality in similar tremolite skarns, commonly in association with norbergite. Dissakisite in the Aldan Shield, southern Yakutia, USSR, occurs in diopside-phlogopite rocks (magnesian skarns) at the Fedorovskoye and Emel'dzhak deposits (Khvostova and Bykova, 1961). Chromian dissakisite occurs in micaceous layers alternating with quartzofeldspathic layers in schist in the Outokumpu mining district, Finland; associated minerals are chromian phlogopite and a spinel rich in Zn and Cr (Treloar and Charnley, 1987). The dissakisite-(Ce) from China is a secondary mineral with magnesian staurolite, pargasite, chlorite, and clinozoisite in corundum-garnet rocks with primary Na-rich phlogopite, zoisite, and apatite (Enami and Zang, 1988). The Trimoun talc deposit in France is reported to host several rare earth element minerals including dissakisite, which occurs as crystals in geodes of dolomite (Moëlo et al., 1974; Piret et al., 1990). The Antarctic dissakisite-(Ce) occurs in marble (this study). Dissakisite reported from other localities may have originated from pegmatite, but we have no details on the parageneses.

The parageneses in Sweden, USSR, China, and Antarctica have several features in common. The host rocks (except the magnetite ores) are (1) highly enriched in Mg relative to Fe such that even the minerals that are normally relatively Fe rich (staurolite, garnet, and spinel) are magnesian, (2) silica undersaturated, and (3) relatively rich in Ca. Another highly magnesian host rock is the French talc deposit. Regarding the magnetite ore occurrence, the subaluminous ferroan dissakisite analyzed by Geijer (1927) possibly comes from the tremolite skarn, whereas allanite in the magnetite ore could be considerably more Fe rich.

In dissakisite-(Ce) from Antarctica, Fe is fractionated relative to Mg more than in spinel and less than in geikielite, and allanite from nearby localities is less magnesian than associated garnet and hercynite (Grew et al., 1989). On the other hand, the dissakisite of Enami and Zang (1988) is more magnesian ($X_{Mg} = 0.91$) than associated garnet (0.85) and staurolite (0.74). Whatever the details of the sequence of Fe-Mg fractionation, allanite and dissakisite tend to be enriched in Fe^{2+} relative to Mg, and magnesian members of the allanite-dissakisite series are probably restricted to associations with phlogopite, diopside, talc, pyrope-rich garnet, magnesian spinel, magnesian ilmenite, and magnesian staurolite.

The partitioning of REE into dissakisite over coexisting apatite is marked (compare Tables 1 and 2). REE substitute into minerals of the epidote group by a different mechanism ($Ca + Al = REE + R^{2+}$) than in apatites ($Ca + P = REE + Si$, $2Ca = Na + REE$), and thus high levels of REE in minerals of the epidote group will not necessarily be linked to concomitant levels in coexisting apatites.

The role of P-T conditions in the parageneses of dissakisite is less obvious than that of compositional factors. Dissakisite-(Ce) appears to be restricted to moderate to relatively high temperatures (approaching 800–850 °C, Enami and Zang, 1988; about 600 °C, this study) and intermediate to high pressures (≥ 11 kbar, Enami and Zang, 1988; ≤ 7 kbar, this study). These two occurrences are similar in that dissakisite-(Ce) at both localities is a secondary mineral formed from a high-temperature and relatively high-pressure assemblage.

Dissakisite-(Ce) may not be a rare mineral in rocks of appropriate bulk composition. Pegmatites with relatively high bulk Mg/Fe ratios and lacking quartz are potential hosts for ferroan dissakisite. In highly magnesian, silica-undersaturated calcareous rocks, dissakisite-(Ce) could be an important carrier of rare earth elements. Marbles and skarns are potential candidates as well as the Mg-Al-rich, Si-Fe-poor rocks characteristic of some deep seated terranes, of which Enami and Zang's (1988) garnet-corundum rock is a prime example.

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