

## Amygdale Titan-phlogopite from Dôzen, Oki Islands

By

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### Introduction

Dôzen volcano is composed of Pliocene alkaline rocks ranging from alkali olivine basalt, through trachybasalt, trachyandesite, tristanite and trachyte, to alkali rhyolite. The volcano has a central cone and a caldera embayed by the somma, and a large number of radial dikes intruded into the somma and the central cone (TIBA, 1975). Some trachybasalt lavas of the somma carry amygdale with phlogopite and calcite, or zeolites. The amygdale phlogopite has a high  $\text{TiO}_2$  content similarly to biotite phenocrysts in tristanites and trachytes as previously reported (TIBA, 1972). In this paper, amygdale titanphlogopite is described, and a method of molecular calculation of mica group is proposed.

### Occurrence

The trachybasalt lava with amygdale phlogopite (NSM-M19408) was taken on a beach near Aoya, Naka-no-shima, Dôzen, Shimane Prefecture.

The rock is brownish gray with a purplish tint and carries abundant spherical (generally about 1 cm or less across) and elongated (several centimeters long) amygdales. Under the microscope the rock is porphyritic with tabular plagioclase phenocrysts. Fine-grained intergranular groundmass consists of plagioclase laths, clinopyroxene prisms or granules, irregular magnetite grains, ilmenite needles, interstitial anorthoclase and phlogopite. Irregular-shaped masses of iddingsite-like material are seen sporadically.

Amygdale phlogopite grows with or without calcite upon the carpet of light orange earthy material (nontronite) which is coating the amygdale. Bright brown flaky crystals (up to 3 mm across) of phlogopite show random orientation in the amygdale (Fig. 1).

### Titan-phlogopite

Amygdale phlogopite was separated by means of Isodynamic magnetic separator and purified by hand picking. Chemical analysis of the mineral is given in Table 1 together with atomic ratios on the anhydrous basis of  $\text{O}=22$ . This phlogopite in-

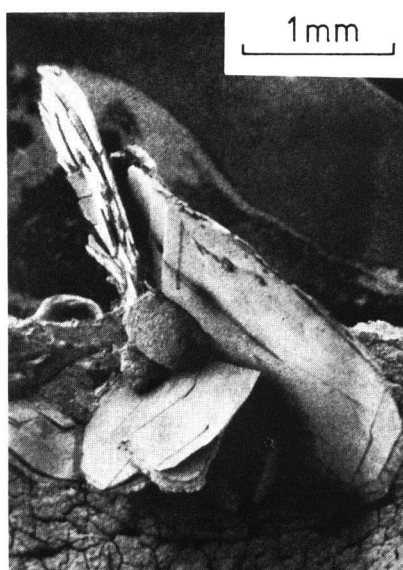


Fig. 1. Scanning electron micrograph of phlogopite flakes grown on the carpet of earthy material (nontronite) in an amygdale.

Table 1. Chemical analysis, atomic ratios (on the anhydrous basis of O=22) and optical properties of titan-phlogopite

SiO <sub>2</sub>	38.97	Si	5.677
TiO <sub>2</sub>	6.45	Al <sup>IV</sup>	2.323
Al <sub>2</sub> O <sub>3</sub>	14.50	Al <sup>VI</sup>	0.165
Fe <sub>2</sub> O <sub>3</sub>	1.94	Fe <sup>3+</sup>	0.213
FeO	7.09	Ti	0.706
MnO	0.12	Fe <sup>2+</sup>	0.864
MgO	15.91	Mn	0.015
CaO	0.96	Mg	3.452
Na <sub>2</sub> O	0.80	Ca	0.150
K <sub>2</sub> O	8.86	Na	0.226
H <sub>2</sub> O <sup>+</sup>	3.47	K	1.647
H <sub>2</sub> O <sup>-</sup>	1.25		
total	100.32		
$\alpha$	1.605	X	pale straw yellow
$\gamma$	1.637	Y=Z	chestnut brown

indicates a considerably high TiO<sub>2</sub> content and a relatively low Fe<sup>3+</sup>/(Fe<sup>3+</sup>+Fe<sup>2+</sup>) ratio. Deficiency of Si in the tetrahedral position is compensated satisfactorily by Al alone.

X-ray powder data of the phlogopite are set in Table 2. In spite of significant deviation from the ideal composition, unit cell parameters of the present phlogopite

Table 2. X-ray powder data for titan-phlogopite

d (Å)	I	Qobs	Qcal	hkl
10.02	100	0.0100	0.0101	(001)
4.995	2	0.0401	0.0403	(002)
4.604	2	0.0472	0.0470	(020)
3.675	8	0.0740	0.0751	(112)
3.326	80	0.0904	0.0907	(003)
3.136	6	0.1017	0.1019	(112)
2.906	5	0.1184	0.1188	(11 $\bar{3}$ )
2.696	2	0.1376	0.1377	(023)
2.621	4	0.1456	0.1455	(200)
2.490	25	0.1613	0.1613	(004)
2.435	2	0.1687	0.1690	(201)
2.203	2	0.2060	0.2060	(222)
2.169	5	0.2126	0.2126	(202), 0.2128 (13 $\bar{3}$ )
1.990	50	0.2525	0.2530	(133), 0.2520 (005)
1.658	10	0.3638	0.3629	(006)
1.537	5	0.4233	0.4234	(060), 0.4232 (33 $\bar{1}$ )
1.530	5	0.4272	0.4277	(135)
1.422	8	0.4945	0.4939	(007)
1.354	6	0.5455	0.5456	(207)
1.300	2	0.5917	0.5890	(117)
1.245	5	0.6452	0.6451	(008)
$a_0$	5.319 Å	$\beta$	99.72°	
$b_0$	9.221 Å			
$c_0$	10.105 Å			

coincide well with those of a synthetic phlogopite (pure magnesian end-member [YODER and EUGSTER, 1954]). The slightly small  $c$  parameter would be due to substitution of Fe for Mg (DEER *et al.*, 1962).

Occurrence of phlogopite in the groundmass and amygdales suggests that the mineral is a later phase of crystallization from trachybasalt magma. On the other hand, titaniferous biotite phenocrysts in tristanites and trachytes (TIBA, 1972) represent one of early phases of crystallization from magmas of intermediate compositions. Fe appears to have crystallized high-Ti phlogopite, though high-temperature and low-pressure crystallization favors Ti incorporation in Fe-free phlogopite (ROBERT, 1976). In the case of Dôzen, presence of Fe must have fixed a considerable amount of Ti in phlogopite. And intimate association of carbonate with phlogopite in amygdales suggests that carbon dioxide in gaseous phase might have affected Ti fixation in phlogopite.

### Molecules of Mica

The fixation of Ti in phlogopite is explained by the substitution  $2\text{Si}^{\text{IV}}\text{Mg}^{\text{VI}} \rightleftharpoons$

$2\text{Al}^{\text{IV}}\text{Ti}^{\text{VI}}$  (OKI, 1961; ROBERT, 1976). High-Ti ( $>0.5\text{Ti a./f.u.}$ ) phlogopites from West Kimberley, Australia, and Murcia, Spain (CARMICHAEL, 1967), and Dôzen, however, never contain enough  $\text{Al}^{\text{IV}}$  to counterbalance completely the octahedral Ti. Actually, titanoeastonite molecule  $\text{K}_2\text{Mg}_{5.5}\text{Ti}_{0.5}\text{Si}_5\text{Al}_3\text{O}_{20}(\text{OH})_4$  (OKI, 1961) and Ti-phlogopite molecule  $\text{K}_2\text{Mg}_5\text{TiSi}_4\text{Al}_4\text{O}_{20}(\text{OH})_4$  (ROBERT, 1976) have too high Al/Ti ratios for the high-Ti phlogopites mentioned above. Then, several molecules including octahedral Ti-bearing ones are considered for a calculation of molecular proportions of mica (Table 3). To simplify the calculation, complete substitutions, *i.e.*,  $\text{K} \rightleftharpoons \text{Na}$ ,  $\text{Al} \rightleftharpoons \text{Fe}^{3+}$  (Cr), and  $\text{Mg} \rightleftharpoons \text{Fe}^{2+}$  ( $\text{Mn}^{2+}$ , Ni), are assumed, and substituted equivalents are not shown in the table.  $\text{Ti}_3$ -phlogopite molecule  $\text{K}_2\text{Mg}_3\text{Ti}_3\text{Al}_8\text{O}_{20}(\text{OH})_4$  is derived from phlogopite molecule  $\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$  by  $3(2\text{Si}, \text{Mg}) \rightleftharpoons 3(2\text{Al}, \text{Ti})$  substitution,  $\text{Ti}_4$ -mica molecule  $\text{K}_2\text{Ti}_4\text{Al}_6\text{Si}_2\text{O}_{20}(\text{OH})_4$  from muscovite molecule  $\text{K}_2\text{Al}_4\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$  by  $4(\text{Si}, \text{Al}^{\text{VI}}) \rightleftharpoons 4(\text{Al}^{\text{IV}}, \text{Ti})$  substitution and  $\text{Ti}_3$ -mica molecule  $\text{K}_2\text{Ti}_3\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$  from phlogopite molecule by  $6\text{Mg} \rightleftharpoons 3\text{Ti}$  substitution.

Molecular proportions of micas are calculated in the following order:

Table 3. Molecules of mica

phlogopite	$\text{K}_2 \text{ Mg}_6$	$\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$
muscovite	$\text{K}_2 \text{ Al}_4$	$\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$
lepidolite	$\text{K}_2 \text{ Li}_4\text{Al}_2$	$\text{Si}_3\text{O}_{20}(\text{OH})_4$
margarite	$\text{Ca}_2 \text{ Al}_4$	$\text{Al}_4\text{Si}_4\text{O}_{20}(\text{OH})_4$
Al-biotite*	$\text{K}_2 \text{ Al}_6$	$\text{Al}_3\text{O}_{20}(\text{OH})_4$
$\text{Ti}_3$ -phlogopite**	$\text{K}_2 \text{ Mg}_3\text{Ti}_3$	$\text{Al}_3\text{O}_{20}(\text{OH})_4$
$\text{Ti}_4$ -mica**	$\text{K}_2 \text{ Ti}_4$	$\text{Al}_6\text{Si}_2\text{O}_{20}(\text{OH})_4$
$\text{Ti}_3$ -mica**	$\text{K}_2 \text{ Ti}_3$	$\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$

\* hypothetical (RUTHERFORD, 1973)

\*\* hypothetical

Table 4. Calculation of molecular proportions of titan-phlogopite from Dôzen

atomic ratios O=22		Ma	Ph	$\text{Ti}_4$ -M	$\text{Ti}_3$ -M
Si	5.677	0.300/5.377	4.331/1.046	0.122/0.924	0.924/0
$\text{Al}^{\text{IV}}$	2.323	0.600/2.101	1.444/0.657	0.366/0.291	0.308/-0.017
$\text{Al}^{\text{VI}}$	0.165				
$\text{Fe}^{3+}$	0.213				
Ti	0.706			0.244/0.462	0.462/0
$\text{Fe}^{2+}$	0.864	4.331	4.331/0		
Mn	0.015				
Mg	3.452				
Ca	0.150	0.150/0			
Na	0.226	1.873	1.444/0.429	0.122/0.307	0.308/-0.001
K	1.647				
molecular prop.		0.6000	5.775	0.488	1.232
molecular %		7.4	71.3	6.0	15.2

Ma = margarite, Ph = phlogopite,  $\text{Ti}_4$ -M =  $\text{Ti}_4$ -mica,  $\text{Ti}_3$ -M =  $\text{Ti}_3$ -mica.

Table 5. Calculation of molecular proportions of phlogopite in peridotite xenolith (AOKI, 1975)

atomic ratios O=22		Ma	Ti <sub>3</sub> -Ph	Ph	Ti <sub>4</sub> -M
Si	5.861	0.074/5.787		5.764/0.023	0.023/0
Al <sup>IV</sup>	1.999	0.148/2.037	0.104/1.933	1.921/0.012	0.066/-0.054
Cr	0.111				
Fe <sup>3+</sup>	0.075				
Ti	0.084		0.039/0.045		0.045/0
Fe <sup>2+</sup>	0.346	5.803	0.039/5.764	5.764/0	
Mn	0.003				
Mg	5.433				
Ni	0.021				
Ca	0.037	0.037/0			
Na	0.105	1.981	0.026/1.955	1.921/0.034	0.023/0.011
K	1.876				
molecular prop.		0.148	0.104	7.685	0.089
molecular %		1.8	1.3	95.8	1.1

Ma = margarite, Ti<sub>3</sub>-Ph = Ti<sub>3</sub>-phlogopite, Ph = phlogopite, Ti<sub>4</sub>-M = Ti<sub>4</sub>-mica.

Table 6. Calculation of molecular proportions of biotite (lepidomelane) from Northern Nigeria (JACOBSON *et al.*, 1958)

atomic ratios		Le	Ma	Ph	Ti <sub>3</sub> -M	Mu	Al-Bi
Si	6.025	0.998/ 5.027	0.056/ 4.971	3.972/ 0.999	0.446/ 0.553	0.553/0	
Al <sup>IV</sup>	1.975	0.250/ 2.539	0.112/ 2.427	1.324/ 1.103	0.148/ 0.955	0.553/ 0.402	0.402/0
Al <sup>VI</sup>	0.284						
Fe <sup>3+</sup>	0.530						
Ti	0.223				0.223/0		
Fe <sup>2+</sup>	3.863	3.972		3.972/0			
Mn	0.056						
Mg	0.053						
Li	0.499	0.499/0					
Ca	0.028		0.028/0				
Na	0.122	1.928	0.250/ 1.678	1.324/ 0.354	0.148/ 0.206	0.184/ 0.022	0.057/ -0.035
K	1.806						
molecular prop.		0.980	0.112	5.296	0.594	0.737	0.228
molecular %		12.3	1.4	66.6	7.5	9.3	2.9

Le = lepidolite, Ma = margarite, Ph = phlogopite, Ti<sub>3</sub>-M = Ti<sub>3</sub>-mica, Mu = muscovite, Al-Bi = Al-biotite.

1. Ca and Li enter into margarite and lepidolite molecules, respectively.

2. If residual  $Si > Mg + 1/2Ti$ , Si is allotted to form phlogopite, then to form Ti<sub>3</sub>-mica and/or Ti<sub>4</sub>-mica according to the amount of Si remaining after phlogopite formation.

2'. When  $Si < Mg + 1/2Ti$ , Si is allotted to form Ti<sub>3</sub>-phlogopite, phlogopite and/or

Ti<sub>4</sub>-mica.

3. If there are still excess Si and Al, they are allotted to form muscovite.

3'. If there is excess Al, it is allotted to form Al-biotite. Examples of the calculation are shown in Tables 4–6. Apart from the question whether all these molecules could be fixed in a single mica structure or not, the present method of calculation gives reasonable proportions without significant excess or deficiency of cations.

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