Magnesio-ferri-fluoro-hornblende from Portoscuso, Sardinia, Italy: description of a newly approved member of the amphibole supergroup

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ABSTRACT

Magnesio-ferri-fluoro-hornblende has the ideal formula ${}^{A}\Box^{B}Ca_{2}{}^{C}(Mg_{4}Fe^{3+})^{T}(Si_{7}Al)O_{22}{}^{W}F_{2}$ (Hawthorne *et al.*, 2012). The holotype sample described in this work occurs as prismatic crystals in yugs of volcanic rocks (Seruci ignimbrites), found along the coast road ~5.5 km northeast of Portoscuso, Cagliari, Sardinia; associated minerals are tridymite, todorokite, magnetite, and hematite. The name and the mineral were approved by the IMA CNMNC (2014-091). Holotype magnesio-ferri-fluoro-hornblende is monoclinic, space group $C^{2/m}$, a = 9.839(5), b = 18.078(9), c = 5.319(3) Å, $\beta = 104.99(3)^{\circ}, V = 913.9(9)$ Å³, Z = 2. The density calculated from the empirical formula is 3.315 g cm^{-3} . In plane-polarized light, magnesio-ferri-fluoro-hornblende is pleochroic, X =pale grey (least), $Y = \text{dark grey (most)}, Z = \text{pale brownish grey (intermediate)}; X^{a} = 47.6^{\circ}$ (β obtuse), $Y \parallel b$, $Z^{\wedge}c = 33.4^{\circ}$ (β acute). It is biaxial negative, $\alpha = 1.669$, $\beta = 1.676$, $\gamma = 1.678$, all ± 0.002 ; $2V_{obs} = 74(1)^{\circ}$, $2V_{calc} = 1.678$, $\gamma = 1.678$, all ± 0.002 ; $2V_{obs} = 74(1)^{\circ}$, $2V_{calc} = 1.678$, $\gamma = 1.678$, all ± 0.002 ; $2V_{obs} = 74(1)^{\circ}$, $2V_{calc} = 1.678$, $\gamma = 1.678$, 56°. The strongest eight lines in the powder X-ray diffraction pattern are [d in Å (I)(hkl)]: 2.711 (100)(151), 8.412 (89)(110), 3.121 (64)(310), 2.553 (61)(202), 3.389 (55)(131), 2.599 (45)(061), 2.164 (36)(261), and 2.738 (34)(331). Electron-microprobe analysis of the refined crystal gave SiO₂ 45.34, Al₂O₃ 6.18, TiO₂ 1.22, FeO 15.24, Fe₂O₃ 6.27, MgO 9.71, MnO 0.78, ZnO 0.06, CaO 10.18, Na₂O 1.35, K₂O 1.15, F 3.22, Cl 0.30, H2Ocalc 0.37, sum 99.95 wt.%. The empirical formula unit, calculated on the basis of 24 (O,OH,F,Cl) apfu with (OH + F + CI) = 2 apfu is: $(Na_{0.15}K_{0.22})_{\Sigma 0.37}(Na_{0.25}Ca_{1.66}Mn_{0.09})_{\Sigma 2.00}(Mg_{2.20}Fe_{1.94}^{2+}Mn_{0.01}Zn_{0.01}Fe_{0.77}^{3+})$ $Ti_{0.13})_{\Sigma 5.01} (Al_{1.11}Si_{6.89})_{\Sigma 8.00}O_{22}[F_{1.55}(OH)_{0.37}Cl_{0.08})_{\Sigma 2.00}.$

Keywords: magnesio-ferri-fluoro-hornblende, amphibole, electron-microprobe analysis, crystal-structure refinement, Sardinia.

Introduction

AMPHIBOLE compositions related to the root-name hornblende, ${}^{A}\square {}^{B}Ca_{2}{}^{C}(Mg_{4}Al)^{T}(Si_{7}Al)O_{22}{}^{W}(OH)_{2}$, are common both in Nature and in the petrological and mineralogical literature. However, not all possible minerals involving the root-name hornblende have been approved by the IMA Commission on New Mineral Nomenclature and

* E-mail:oberti@crystal.unipv.it DOI: 10.1180/minmag.2016.080.008 Classification (IMA-CNMNC). Therefore, after approval of the new rules for amphibole classification and nomenclature (Hawthorne *et al.*, 2012), we have initiated a systematic search to identify and characterize suitable samples to be recognized as the official holotypes of the hornblende-related compositions not yet approved as mineral species. This is the case for magnesio-ferri-fluorohornblende.

A rock sample provided by Luigi Chiappino, an Italian mineral collector in close contact with the academic mineralogical community, afforded us the opportunity to characterize the holotype of

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FIG. 1. A typical crystal of magnesio-ferri-fluoro-hornblende from the sample studied from Portoscuso, Sardinia. The crystal is ~1.2 mm long.

magnesio-ferri-fluoro-hornblende. Its complete mineral description is reported in this paper. It was approved by the IMA-CNMNC (2014-091). The holotype sample has been deposited at the Mineralogical Museum of the Department of Earth and Environmental Sciences of the University of Pavia (Italy) under the code 2014-01. Further samples are available in the collection of Luigi Chiappino (chiappino.checkpoint@hotmail.it).

Mineral data

Occurrence and paragenesis

Holotype magnesio-ferri-fluoro-hornblende was collected in June 2010 by Luigi Chiappino along the coast road ~5.5 km northeast of Portoscuso. Cagliari, Sardinia, Italy (39°14'57.4"N, 8°24'19.4" E). In this area, the Miocene (15–16 Ma) rhvolitic ignimbrite of Seruci crops out extensively; it is densely welded, and brownish-to-grey in colour (Assorgia et al., 1990, 1992; Ottelli and Perna, 1993; Morra et al., 1994). This pyroclastic formation is characterized by the presence of abundant flattened (fiamme) juvenile pumiceous fragments frequently affected by devetrification processes and vapour-assisted re-crystallization with large typical trydimite crystals and subordinate mafic minerals. In this context, amphibole crystals occur in vugs, either isolated from or perched on tridymite. Associated minerals are tridymite, todorokite, magnetite and hematite.

The refined and analysed crystal of this work has the code 1231 in the amphibole database of the CNR-IGG Pavia.

Appearance, physical and optical properties

Magnesio-ferri-fluoro-hornblende from Portoscuso has a prismatic habit, and may reach 3 mm in length (Fig. 1). Striations parallel to the direction of elongation are common on prism faces. Magnesio-ferri-fluorohornblende is dark brown in colour; the lustre is vitreous, transparent, and fluorescence is not present. The tenacity is brittle and single crystals show perfect cleavage parallel to {110}. The density (calculated from the unit formula and cell dimensions) is 3.315 g/cm³. A spindle stage was used to orient a crystal for measurement of indices of refraction and 2V by extinction curves (Bartelmehs et al., 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a singlecrystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, magnesio-ferri-fluoro-hornblende is pleochroic X =pale grey (least), Y = dark grey (most), Z = palebrownish grey (intermediate), $X \wedge a = 47.6^{\circ}$ (β obtuse), $Y \parallel b$, $Z \wedge c = 33.4$ (β acute). It is biaxial negative with indices of refraction $\alpha = 1.669$, $\beta =$ 1.676, $\gamma = 1.678$, all ± 0.002 , measured with gel-filtered Na light ($\lambda = 589.9$ nm). The significant discrepancy between 2V (meas.) = $74(1)^{\circ}$ and 2V (calc.) = 56° is due to the fact that $\beta = 1.676(2)$ and $\gamma = 1.678(2)$ are very close and the difference is very imprecise.

X-ray diffraction and crystal-structure refinement

The crystal of magnesio-ferri-fluoro-homblende selected for data collection and structure refinement

a (Å)	9.839(5)	Crystal size (mm)	$0.30 \times 0.15 \times 0.55$
b(Å)	18.078(9)	Crystal colour	Dark brown
c (Å)	5.319(3)	Total no. of reflections	2715
β (°)	104.99(3)	No. unique reflections	1390
$V(Å^3)$	913.9(9)	No. observed reflections $(I > 3\sigma_I)$	1013
Space group	C2/m	θ range (°)	2-30
Z	2	$R_{\rm sym}$ (%)	2.70
D_{calc} (g cm ⁻³)	3.315	$R_{\rm obs}$ (%)	2.30
μ MoK α (cm ⁻¹)	32.8	$R_{\rm all}$ (%)	3.92

TABLE 1.	Miscella	aneous i	nf	ormatio	n fe	or magne	sio-	ferr	i-f	luoro-l	hornl	ol	end	e f	from	Portosc	uso.
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is \sim 300 µm x 150 µm x 150 µm in size. It is identified with the code 1231 in the CNR-IGG amphibole data base in Pavia. Data collection was carried out on a Philips PW1100 four-circle diffractometer using graphite-monochromatized MoK α X-radiation (λ = 0.7107 Å). Unit-cell parameters were calculated from least-squares refinement of the d* values obtained for 60 rows of the reciprocal lattice by measuring the centre of gravity of each reflection and of its antireflection in the 20 range -70° to 70° . Two monoclinic equivalents were collected in the 20 range 4-60°, absorption and Lp correction were applied and equivalent reflections were merged to give 1390 independent reflections ($R_{sym} = 2.70\%$). Only the 1013 reflections with $I > 3\sigma_I$ were considered as observed during unweighted full-matrix least-squares refinement on *F*. Scattering curves for fully ionized chemical species were used at sites where chemical substitutions occur; neutral scattering curves were used against ionized scattering curves at the other sites, namely *T* and anion sites [except O(3)]. More details of the refinement strategy are given by Oberti *et al.* (1992). Full-matrix least-squares refinement on $I > 3\sigma_I$ gave $R_{obs} = 2.30\%$ and $R_{all} = 3.92\%$.

Unit-cell dimensions and details of the crystallographic study are reported in Table 1. The *a:b:c* proportions calculated from the unit-cell parameters are 0.544:1:0.294. Table 2 lists atom coordinates and anisotropic-displacement parameters, and Table 3 gives selected interatomic distances and parameters related to the conformation of the double chain of tetrahedra. The measured structure factors have been

TABLE 2. Atomic coordinates, refined site-scattering values (ss, epfu), atom-displacement parameters (B_{eq} , Å²; $\beta_{ii} \times 10^4$) for magnesio-ferri-fluoro-hornblende from Portoscuso.

Site	SS	x/a	y/b	z/c	B _{eq}	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β ²³
O(1)		0.11024(20)	0.08735(10)	0.21700(37)	0.86(4)	24	7	72	3	8	$\overline{2}$
O(2)		0.11934(20)	0.17161(11)	0.72864(36)	0.93(4)	24	8	74	0	6	ī
0(3)	17.56(10)	0.10456(27)	0	0.71200(47)	1.19(6)	46	8	75	_	14	_
O(4)	× ,	0.36559(22)	0.24943(11)	0.79359(38)	1.07(4)	37	7	91	$\overline{4}$	16	ī
O(5)		0.34844(22)	0.13600(11)	0.10233(40)	1.22(4)	30	11	104	2	10	11
O(6)		0.34449(22)	0.12020(10)	0.59232(40)	1.08(4)	28	9	100	0	12	5
O(7)		0.33836(30)	0	0.29549(57)	1.19(6)	32	8	137	_	18	_
T(1)		0.28243(8)	0.08463(4)	0.29971(14)	0.59(1)	18	4	48	ī	1	0
T(2)		0.29098(7)	0.17101(4)	0.80847(13)	0.59(1)	18	5	46	ī	6	0
M(1)	33.74(17)	0	0.08863(5)	¹ / ₂	0.78(2)	22	8	48	_	10	_
M(2)	45.39(14)	0	0.17867(3)	0	0.70(2)	20	5	66	_	8	_
M(3)	16.31(6)	0	0	0	0.63(3)	24	4	43	_	0	_
M(4)	36.54(22)	0	0.27894(4)	$1/_{2}$	0.92(2)	32	6	91	_	31	_
M(4')	0.68(10)	0	0.2465(24)	$1/2^{-1}$	1.1(6)						
A(m)	5.62(11)	0.0240(12)	¹ / ₂	0.0590(18)	3.3(3)	142	17	400	_	197	_
H	0.72(17)	0.188(16)	0	0.846(29)	1.0						

epfu - electrons per formula unit.

T(1)-O(1) T(1)-O(5) T(1)-O(6) T(1)-O(7)	1.637(2) 1.655(2) 1.648(2) 1.628(1)	T(2)-O(2) T(2)-O(4) T(2)-O(5) T(2)-O(6)	1.631(2) 1.608(2) 1.645(2) 1.660(2)
<t(1)-o></t(1)-o>	1.642	< <i>T</i> (2)–O>	1.636
$ \begin{array}{c} M(1) - O(1) \times 2 \\ M(1) - O(2) \times 2 \\ M(1) - O(3) \times 2 \end{array} $	2.071(2) 2.090(2) 2.073(2)	$M(2)-O(1) \times 2$ $M(2)-O(2) \times 2$ $M(2)-O(4) \times 2$	2.142(2) 2.087(2) 1.973(2)
<m(1)-o></m(1)-o>	2.078	< <i>M</i> (2)–O>	2.067
$M(3)-O(1) \times 4$ $M(3)-O(3) \times 2$	2.087(2) 2.054(3)	<i>M</i> (4)−O(2) ×2 <i>M</i> (4)−O(4) ×2	2.426(2) 2.349(2)
< <i>M</i> (3)–O>	2.076	M(4)–O(5) ×2 M(4)–O(6) ×2	2.726(2) 2.509(2)
$M(4')-O(2) \times 2$ $M(4')-O(4) \times 2$	1.988(2) 2.294(2)	< <i>M</i> (4)–O>	2.502
$M(4') - O(5) \times 2$ $M(4') - O(6) \times 2$	3.095(2) 2.962(2)	$\begin{array}{l} A(m) - \mathrm{O}(5) \times 2 \\ A(m) - \mathrm{O}(5) \times 2 \end{array}$	3.047(7) 2.986(6)
< <i>M</i> (4′)–O>	2.585	$A(m) - O(6) \times 2$ A(m) - O(7)	2.932(7) 2 471(10)
T(1)-O(5)-T(2) T(1)-O(6)-T(2)	136.4(1) 139.8(1)	A(m) = O(7) A(m) = O(7) A(m) = O(7)	3.349(10) 2.591(10)
T(1) - O(7) - T(1) O(5) O(6) O(5)	140.0(2)	< <i>A</i> (<i>m</i>)–O>	2.927
0(6)-0(7)-0(6)	107.0(1) 108.5(1)	<i>M</i> (1)– <i>M</i> (2)	3.118

TABLE 3. Selected interatomic distances (Å) and angles (°) in magnesio-ferri-fluoro-hornblende from Portoscuso.

deposited with the Principal Editor of *Mineralogical Magazine* as a cif file, and are available from www. minersoc.org/pages/e_journals/dep_mat.html.

X-ray powder-diffraction data (Cu $K\alpha$, λ = 1.54178 Å) were obtained using the *XPREP* utility of *SAINT* (Bruker, 2003), which generates a 2D powder diffractogram (Debye-Scherrer technique) starting from the F_{obs} collected on the single crystal and taking into account solely the information concerning the unit-cell dimensions and the Laue symmetry. No Lorentz and polarization correction was applied. The resulting data are given in Table 4.

Chemical composition

The crystal of magnesio-ferri-fluoro-hornblende used for the crystallographic study was embedded

in epoxy and analysed by electron microprobe using a Cameca SX-100 operating in wavelengthdispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 µm, peak-count time 20 s and background-count time 10 s. The following standards and crystals were used for Ka X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LPET; Fe: favalite, LLiF; Mn: tephroite, LLiF; Mg: periclase, LTAP; Al, corundum, TAP; K: orthoclase, LPET; Na: jadeite, TAP; F: fluoro-riebeckite, LTAP; Cl: tugtupite, LPET; Zn: gahnite, LLiF. Data reduction was undertaken using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The elements V, Cr and Ni were found to be below the detection limit. The average of 10 point analyses is given in Table 5, together with a formula based on stoichiometric constraints and SREF (single-crystal structure refinement) results. The H₂O content compatible with F and Cl analyses is guite low (maximum 0.37 atoms per formula unit, apfu). Because no clear indication of the presence of the oxo component was found, the formula was recalculated based on 24 anions and $^{W}(OH + F + Cl) = 2$ apfu. giving

$$\label{eq:alpha} \begin{split} &^{A}(Na_{0.15}K_{0.22})_{\Sigma0.37}{}^{B}(Na_{0.25}Ca_{1.66}Mn_{0.09})_{\Sigma2.00} \\ &^{C}(Mg_{2.20}Fe_{1.94}^{2+}Mn_{0.01}Zn_{0.01}Fe_{0.72}^{3+}Ti_{0.13})_{\Sigma5.01} \\ &^{T}(Al_{1.11}Si_{6.89})_{\Sigma8.00}O_{22}{}^{\textit{W}}[F_{1.55}(OH)_{0.37}Cl_{0.08})_{\Sigma2.00}. \end{split}$$

The compatibility index $[1 - (K_P/K_C)]$ is 0.001 (superior). The simplified end-member formula is ${}^{B}Ca_{2}{}^{C}(Mg_{4}Fe^{3+})^{T}(Si_{7}Al)O_{22}{}^{W}F_{2}$, which requires SiO₂ 49.67, Al₂O₃ 6.02, Fe₂O₃ 9.43 MgO 19.04, CaO 13.24, F 4.49, O = F -1.89, total 100.00 wt.%.

Site populations and crystal-chemistry

The agreement between the observed (from SREF) and calculated (from EMPA) group site-scattering values (~3.2%) is good but not excellent, and reflects the presence of minor compositional heterogeneity in the crystal (as shown by the tabulated ranges for wt.% oxides). In particular, SREF (which provides a composition averaged over the whole crystal) would suggest a slightly lower amount of ^TAl and ^CFe. Site populations (Hawthorne *et al.*, 1995) were calculated based on present knowledge of amphibole crystal-chemistry, and are reported in Table 6. Tetrahedrally-coordinated Al is ordered at the *T*(1) site (Oberti *et al.*, 1995, 2007, and highly charged C cations are

Irel	d(calc)	h k l	I _{rel}	d(calc)	h k l	I _{rel}	d(calc)	h k l	I _{rel}	d(calc)	h k l
21	9.039	020	22	2.941	221	6	2.223	$\bar{2}$ 4 2	4	1.852	4 4 2
89	8.412	110	17	2.804	330	8	2.184	171	1	1.828	281
1	5.081	130	34	2.738	<u>3</u> 31	36	2.164	261	5	1.808	0 10 0
20	4.914	$\bar{1}$ 1 1	100	2.711	151	17	2.049	202			191
4	4.752	200	45	2.599	061	23	2.018	351	6	1.753	512
19	4.519	040	61	2.553	$\bar{2} 0 2$	7	2.002	370	4	1.720	$\bar{5} 5 1$
9	4.470	021	3	2.471	022	3	1.976	<u>3</u> 71	13	1.694	$\overline{1}$ 3 3
4	4.206	220	3	2.457	$\bar{2}$ 2 2			4 2 2			$\bar{2}$ 8 2
2	3.997	111	2	2.433	$\overline{1}$ 3 2	5	1.965	190	8	1.683	023
5	3.896	$\bar{1}$ 3 1	2	2.408	311	3	1.946	$\bar{3}$ 5 2			<u>3</u> 91
2	3.696	$\bar{2} 2 1$	5	2.381	350	3	1.926	421	26	1.649	461
55	3.389	131	34	2.342	<u>3</u> 51	5	1.890	510	9	1.638	480
24	3.275	240	14	2.327	$\bar{4} 2 1$	6	1.880	$\bar{4} 6 1$	13	1.619	1 11 0
64	3.121	310	16	2.304	$\bar{1}$ 7 1	8	1.868	$\bar{1}$ 9 1	25	1.587	ī 5 3
3	3.031	311	22	2.290	<u>3</u> 12			242			600
3	3.015	060	4	2.254	331	4	1.852	$\bar{1}$ 7 2	8	1.555	402

TABLE 4. Powder X-ray data for magnesio-ferri-fluoro-hornblende from Portoscuso.

The eight strongest lines are in bold.

ordered at the M(2) site, as expected for amphibole compositions with no oxo-component (Hawthorne and Oberti, 2007). The resulting agreement between the observed and calculated mean bonddistances for the T(1) and M(1-3) sites is quite satisfactory. As expected for a F-dominant composition (Hawthorne *et al.*, 1996), the A cations are fully ordered at the A(m) site.

TABLE 5. Chemical composition and unit formula for magnesio-ferri-fluoro-hornblende from Portoscuso.

Oxide	wt.%	Range	Oxide	wt.%	Range		apfu		apfu
SiO ₂ TiO ₂	45.34(48) 1.22(6)	44.71–46.54 1.14–1.29	H ₂ O** F	0.37 3.22(26)	2.80-3.61	Si Al	6.888 1.107	Mn ²⁺ Na	0.091 0.252
Al_2O_3	6.18(15)	5.99-6.48	Cl	0.30(5)	0.26-0.35	Sum T	7.995	Ca	1.657
Fe ₂ O ₃ *	6.27		O = F,Cl	-1.42		${\rm Ti}^{4+}$	0.134	Sum B	2.000
FeO* [FeO] _{tot}	15.24 [20.88(49)]	20.36-22.02	Total	99.95		Fe ³⁺ Fe ²⁺	0.717 1.936	K Na	0.223 0.146
MnO ZnO MgO CaO	0.78(3) 0.06(5) 9.71(23) 10.18(29)	0.72–0.85 0.00–0.14 9.31–10.15 9.43–10.50	Group site C B	scattering (ep obs (SREF) 95.44 37.22	fu) calc (EMP) 98.72 38.19	Mg Zn Mn ²⁺ Sum C	2.197 0.007 0.009 5.000	Sum A F ⁻ OH ⁻ Cl ⁻	0.369 1.547 0.376 0.077
Na ₂ O	1.35(47)	0.71-1.94	А	5.62	5.84			Sum W	2.000
K ₂ O	1.15(4)	1.04-1.19	Total	138.28	142.75				

*FeO:Fe₂O₃ ratio calculated from single-crystal structure-refinement results.

**Calculated based on 24 (O, OH, F, Cl) with (OH + F + Cl) = 2 apfu.

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		Site s	cattering pfu)	Bond distance (Å)		
Site	Site population (apfu)	Refined	Calculated	Refined	Calculated	
T(1) T(2)	2.89 Si + 1.11 Al 4 Si			1.642	1.652	
M(1) M(2)	$\begin{array}{l} 1.22 \text{ Mg} + 0.78 \text{ Fe}^{2+} \\ 0.36 \text{ Mg} + 0.79 \text{ Fe}^{2+} + 0.72 \text{ Fe}^{3+} + 0.13 \text{ Ti} + 0.01 \text{ Zn} \end{array}$	33.74 45.39	34.92 46.74	2.078 2.067	2.076 2.063	
<i>M</i> (3)	$0.62 \text{ Mg} + 0.37 \text{ Fe}^{2+} + 0.01 \text{ Mn}$	16.31	17.31	2.076	2.076	
C cations		95.44	98.97			
B cations A cations W anions	0.25 Na + 1.66 Ca + 0.09 Mn 0.15 Na + 0.22 K 1.55 F + 0.37 OH + 0.08 Cl	37.22 5.62	38.20 5.83			

TABLE 6. Site populations in magnesio-ferri-fluoro-hornblende from Portoscuso.

The disordered distribution of Fe^{2+} between the M(1), M(2) and M(3) sites is in accord with relatively high-*T* conditions of crystallization (Oberti *et al.*, 2007).

The presence of magnesio-ferri-fluorohornblende relatively poor in OH, magnetite and hematite in a cavity in an ignimbrite (a felsic rock) provides an excellent example of the mechanism proposed by Czamanske and Wones (1973). These authors showed that as a result of the preferential loss of H_2 from pockets of aqueous fluid in a cooling felsic igneous rock, the fugacity of oxygen (which cannot diffuse away so easily) increases markedly. Iron is consumed to form magnetite and hematite, which causes magnesium to become dominant in mafic minerals as a consequence.

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