MINERALOGICAL STUDY OF KAERSUTITE IN THE VOLCANIC NODULE AT EIFEL, W. GERMANY

SACHINATH MITRA

ABSTRACT

Some lapilli and bombs occurring in the ash ejecta around Eifel in Germany were investigated by the author and one such contained pitch-black shining crystal-aggregates, which on detailed study were found to contain kaersutite, having a chemical formula obtained by wet chemistry as: $(Si_{5.7} Al_{2.3})$ $(Al_{0.2} Ti_{0.4} Fe^{3+}_{0.5} Mn_{0.01} Mg_{3.2})$ $(Ca_{2.0} Na_{0.5} K_{0.4} P_{0.01})$ $(O, OH, F)_{32} \cdot Fe^{2+}$ and Fe^{3+} contents determined by MÖSSBAUER were different from chemical data and are in the ratio of 73 : 27.

High content of Al_2O_3 (3.87—10.84 wt. %) with Tschermak's component ranging from 5.9 to 18.4 mol. p.c. in clino-pyroxenes in the wehrlite and clinopyroxenite inclusions in the volcanics of Eifel region suggest the parent magmas to be alkali-basalt in composition. The chemistry of kaersutite suggests that the crystallization took place in hydrous condition in the lowest part of the crust.

INTRODUCTION

Eifel region in W. Germany is one of the major oft-visited places for geologists, interested in Germany's geology, volcanism or upper mantle studies. The lapilli and nodules ejected out by volcanism at Eifel have become the subject of intensive studies of many groups of workers [AOKI and KUSHIRO, 1968; FRECHEN, 1948, 1963; ROSS et al., 1954; WHITE, 1963] involved in the studies on the mineralogy and geochemistry of the upper mantle.

Studies on the ultramafic inclusions in volcanic effusives, collected from continental, circum-oceanic and oceanic regions indicated that they are broadly of two groups occurring in two types of rocks assemblages: one with extremely silica-undersaturated alkali-basalts such as olivine-nephelinite, nepheline-basanite, and the other are moderately undersaturated alkali-basalt such as olivine-basalt, hawaiite and ankaramite [WHITE, 1966]. Inclusions in the former are generally of lherzolite group and those in the other are of dunite, wehrlite, clinopyroxenite and feldspathic peridotite, likely to be formed by crystal accumulation from alkali-basalt magma. Those of lherzolite may be xenolithic fragments of heterogeneous upper mantle materials, which are not capable of generating basalt magmas [AOKI and KUSHIRO, 1968; WHITE, 1966]. Both the two groups of inclusions have been reported from the tuff from Eifel, W. Germany.

While searching for such nodules in the ash ejecta around a volcanic cone at Eifel (Laachersee) in a team of geoscientists in the summer of 1968 *(Fig. 1)* the author found a nodule (with about 12 cm as major axis and 8 cm minor axis) containing pitch-black mineral with strong shining cleavages. A part of the bomb has been investigated by the present author and the rest was left at the Mineralogical Institute, Heidelberg.
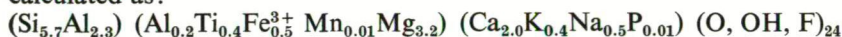
Fig. 1. Geoscientists searching (September, 1968) for volcanic inclusions in the loose tuffs of Eifel. The low angle stratification of ash is conspicuously seen in a nearly vertical exposure

Mineralogical studies of the black minerals is presented in this paper but details of mineralogy and chemistry of the associated ash and other inclusions in the volcanics of the area have not been dealt with by the author except citing some relevant references to other workers' observations. It should be noted here that the Laachersee volcanic province is distinctly different from West Eifel, while both being notable for richness in ultrabasic nodules the former is more abundant in felsic volcanics.

MINERALOGY

With a brown coconut-like shell of ash the nodule contains inside pitch-black large (almost as large as the length of the nodule) crystals of hornblende with angular interpenetrating grain boundaries between subhedral crystals. The chemical composition of a clean cleaved block, of this mineral, crushed to 100 mesh and separated from ore minerals by Franz Isodynamic Magnetic Separator, is shown in Table 1. In this analysis the sample was fused with bisulfate before wet chemical treatment. On the basis of 24 oxygens (with F and OH replacing oxygens) the formula was calculated as:

$(Si_{5.7}Al_{2.3})$ $(Al_{0.2}Ti_{0.4}Fe^{3+}_{0.5} Mn_{0.01}Mg_{3.2})$ $(Ca_{2.0}K_{0.4}Na_{0.5}P_{0.01})$ $(O, OH, F)_{24}$

A comparison of this composition with a hornblende from hornblende-clinopyroxene and kaersutite from a cognate xenolith in trachyte, Japan is also presented in Table 1. Optical study shows dark brown equal absorption along Y and Z direction changing to lighter brown colour in X direction.

$$N_x = 1.660$$
$$N_y = 1.703$$
$$N_z = 1.722$$

$N_z - N_x = 0.062$ and $2V = 68°$ (determined by A. Roy). The Fe^{3+} ratio with Fe^{2+} per formula unit in Eifel sample is three times more than in the Hastings country sample. Mössbauer studies discussed latter give this $Fe^{2+} : Fe^{3+}$ ratio as 73:27 (Table 2), which is more conformable with Scoon's 79:21 and Aoki's 71:29 ratios (from Table 1).

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TABLE 1

*Chemical composition (wt%) of volcanic kaersutite (I) from Eifel and
its comparison with hornblende (II) from hornblende clinopyroxenite from the same
volcanic suites (AOKI and KUSHIRO, 1968) and kaersutite (III) from cognate
xenolith in trachyte, Japan*

Oxides	I	II	III
SiO_2	38.79	42.40	39.68
Al_2O_3	14.73	12.78	12.81
TiO_2	4.02	2.59	7.12
Fe_2O_3	4.55	3.41	4.04
Cr_2O_3	...	0.42	
FeO	5.15	5.42	8.79
MnO	0.06	0.14	0.16
MgO	14.52	15.53	11.22
CaO	12.51	10.70	11.06
Na_2O	1.71	2.53	3.37
K_2O	2.32	1.58	1.04
P_2O_5	0.016		
H_2O^+	1.82	2.29	0.78
H_2O^-	nil	0.05	0.15
Others (F, etc.)	—		0.33
Total	100.196	99.84	100.55

Number of ions on the basis of 24 (O, OH, F, Cl)

	I		II		III	
Si	5.65	} 8.00	6.13	} 8.00	5.937	} 8.00
Al	2.35		1.87		0.063	
Al	0.18		0.31		0.197	
Ti	0.44		0.28		0.801	
Fe^{3+}	0.50		0.37		0.454	
Fe^{2+}	0.63	} 4.907	0.66	} 5.04	1.000	} 5.07
Mg	3.15		3.35		2.501	
Mn	0.007		0.02		0.020	
Cr^{3+}	n.d.		0.05			
Ca	1.95		1.66		1.773	
Na	0.48	} 2.88	0.71	} 2.66	0.976	} 2.95
K	0.44		0.29		0.198	
P	0.01		...			
OH	...		1.81		0.778	} 0.93
F			...		0.156	
Analyst	B. P. GUPTA		K. AOKI and I. KUSHIRO		K. AOKI	

TABLE 2

*[57]Fe hyperfine parameters of volcanic hornblende (kaersutite) from Eifel
(χ^2 of the fit being 0.65 with 400 degrees of freedom)*

Oxidation state	Quadrupole splitting (mm/s)	Isomer shift* (mm/s)	fwhm (mm/s)	% of Total Fe
Fe^{2+}	2.37±0.11	1.24±0.12	0.75±0.13	73
Fe^{3+}	0.67±0.17	0.30±0.19	0.53±0.16	27

* With respect to 99.999% pure Fe-metal.

Thin bar-like inclusions of ilmenite of nearly equal length and with translucent to transparent patches (rutile or leucoxene phases?) occur in an orderly fashion *(Figs. 2 and 3)* aligned parallel to certain crystallographic phases and running along another plane. In some sections two sets of exsolution lamellae align themselves to make acute angles (30°—45°) *(Figs. 2 and 3a)*. Exsolution lamellae reported from Iki Island, Japan, lie parallel mainly to the *c*-axis and sometimes to *a*-axis in (010) [AOKI, 1970].

However, the Ti content in this kaersutite (0.4 Ti per formula unit or $TiO_2 = 4.02\%$) falls slightly shorter than as stipulated earlier to be around 5% TiO_2 (i.e. 0.5 to 1.0 atoms per formula units) *(ibid)*.

The $Fe^{3+} : Fe^{2+}$ ratio per formula unit in Eifel sample is 5:6 but ^{57}Fe Mössbauer studies as discussed later give this ratio as 73:27 (Table 2), which is more conform-
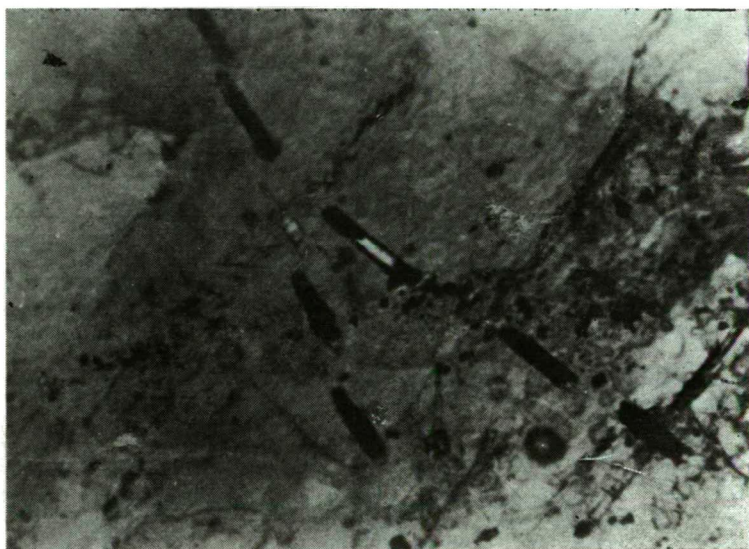

Fig. 2. A microphotograph of volcanic hornblende with Fe—Ti-oxide exsolution laths, some being partly or fully translucent
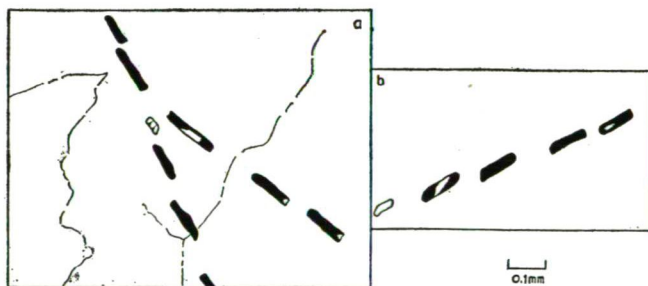

Fig. 3. Sketch showing the nature of ilmenite exsolution along some crystallographic planes. In some sections (a) the bifurcation of the alignment of laths are predominantly seen, cutting across some kaersutite zones showing different absorption characteristics. In some sections (b) only one set of exsolutions

able with AOKI's 71:29 ratios obtained from cognate xenolith in trachyte, Japan (Table 1).

The high $Fe^{3+}:Fe^{2+}$ ratio observed in silicate mineral analyses by wet chemistry is primarily due to two reasons: (1) oxidation of the minerals in post crystallization stage, during subaerial or submarine placement and (2) oxidation after collection of the sample and during treatment for wet chemical analysis.

$Fe^{3+}:Fe^{2+}$ ratios in kaersutites emplaced in subaerial volcanic rocks are higher than those in the submarine lavas etc. and often they are oxidized to oxy-kaersutites. But this sample is less oxidized to be called an oxykaersutite, which needs to have the ratio of about 2 [AOKI, 1970]. However, no clue for estimating the original $Fe^{3+}:Fe^{2+}$ ratio at the time of crystallization was available to the author.

For the sample as collected, the author is inclined to accept the Mössbauer data for the Fe^{2+} and Fe^{3+} contents in preference to wet chemical analyses. No warranted chemical method of Fe^{2+}, Fe^{3+} determination in silicates exists because some part of Fe^{2+} in the sample gets oxidized to Fe^{3+} during grinding in atmospheric air, fusion, dissolution and even during titration or later treatment. Mostly we obtain Fe^{3+} values at the cost of Fe^{2+}. By Mössbauer studies this problem is solved to a great extent (although Fe^{2+} oxidation while grinding and during sample pre-paration cannot be totally ruled out) and the distribution of Fe^{2+} and Fe^{3+} at M_1, M_2, M_3 and M_4 sites has been determined with a discussion on the structural characteris-tics of this mineral. The structural description of the amphibole group of minerals as relevant for understanding the stereochemistry of this mineral is discussed below [BURNS, 1970, p. 99].

There are three sets of six-fold co-ordination designed as M_1, M_2 and M_3 and one of six to eight-fold co-ordination, designed as M_4. Cations in the two M_1 and one M_3 positions are each co-ordinated to four oxygen ions and two hydroxyl ions. The OH-groups are in cis arrangement in the M_1 sites and trans in the M_3 site. Cations in the M_2 positions are surrounded by six oxygen ions and oxygen ions surrounding the M_1, M_2, M_3 sites are linked to one silicon atom. Cations in M_4 positions are preferentially filled by Ca, Na etc. and are surrounded by four oxygen ions each linked to one silicon atom and two to four oxygen atoms which are each shared by two silicon atoms. The octahedra about M_1, M_2 and M_3 positions are almost regular and the cation sites are centrosymmetric, whereas the M_4 co-ordination site is very distorted and has C_{2v} symmetry and cations here do not lie at the centre of symmetry of the site. This M_4 site and orthopyroxene M_2 sites resemble one another in the nature of oxygen ligands and the distortion of co-ordination sites. This is linked with the Crystal Field Stabilization Energies (CFSE) of Fe^{2+} at these sites.

The amount of Fe entering in some eight-fold co-ordinated M(4) site and the Si I and Si II tetrahedral sites are negligible. Normally, electrical neutrality is main-tained by substituting Si in the tetrahedral site. Fe^{3+} may, however, proxy for Al^{3+} when in sufficient amount. The Mössbauer spectra (Fig. 4) suggests that Fe^{3+} is occurring in octahedral sites. HUCKENHOLZ [1971] have shown that significant Fe^{3+} can enter into tetrahedral sites in the related diopside structure. It is possible that even when Al is present in excess of what are required for filling Si I and Si II sites, randomisation of Al and Fe^{3+} among M_2 and tetrahedral sites could occur at high temperature in the volcanic condition.

^{57}Fe Mössbauer spectrum [for details of the instrumental set-up etc. MITRA and BANSAL, 1975] of the sample obtained with a 512 multichannel analyser at room temperature is shown in Fig. 4. Since the line-width of the low velocity peak is much
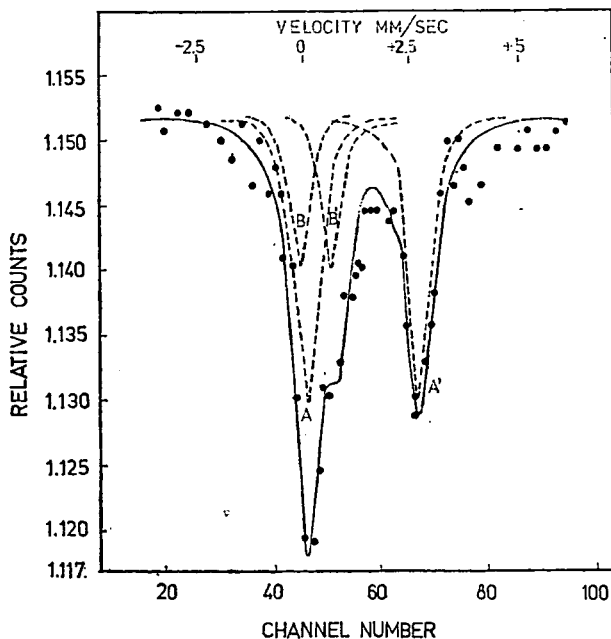
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Fig. 4. Mössbauer spectrum of ^{57}Fe in volcanic hornblende from Eifel, W. Germany

higher than usual the spectrum was least-square fitted to two pairs of Lorentzian lines *AA'* and *BB'*, with constrains that the widths and intensities of the individual lines of a doublet are equal. A χ^2 value of 0.65 was obtained for this fit with 400 degrees of freedom.* Since enough Ca, Na and K (totalling to 2.9 per formula unit) are present to fill the M_4 site, most of the iron is assumed to fill up the remaining M_1, M_2 and M_3 sites [SEMET, 1973]. Since the environment at these three sites are nearly identical the hyperfine parameters are nearly the same and it becomes difficult to resolve the contributions due to individual sites. Although some workers [GREAVES *et al.*, 1971] have resolved these in some cases of actinolites with χ^2 values above 500 (Table 3), the three sites in the sample investigated are considered to give rise to an apparent single pair of lines for both Fe^{2+} and Fe^{3+}. The line-widths obtained are larger than those expected for individual sites, which again shows that there is overlap of two or three sites with nearly equal isomer shifts and quadrupole splittings. Thus the doublets AA' and BB' have been assigned to Fe^{2+} and Fe^{3+} at the M_1, M_2, M_3 sites. The isomer shifts and quadrupole splittings are listed in Table 2 along with errors. The percentage of each iron species are rough estimates calculated by assuming

* The χ^2 values obtained in Mössbauer spectroscopy are frequently higher than one would expect because the function (Lorentzian) used is not absolutely correct. Peaks may deviate from Lorentzian shapes by order-disorder phenomena where they may be distorted by a number of small variations in the electronic state of the absorbing atoms due to environmental fluctuations. Other factors which affect the χ^2 value include instrumental drift, counting geometry, cosine effects, and the proportion of the spectrum computed as being in zero-absorption base-line.

TABLE 3

^{57}Fe *hyperfine parameters in other amphiboles*

Species	Oxidation state	Sites	Quadrupole splitting (mm/s)	Isomer shift (mm/s)	Ref.
Actinolite	Fe^{2+}	M_2	1.89—2.03	1.13—1.16	BANCROFT et al. [1967]
		M_1, M_3	2.81—2.82	1.15—1.16	
Actinolite	Fe^{2+}	M_1	2.89	1.14	Sp. No. In GREAVES
		M_2	1.91	1.14	14.785 et al. [1971]
		M_3	2.57	1.12	
	Fe^{3+}	(M_1, M_2, M_3)	0.53	0.28	
Actinolite	Fe^{2+}	M_1	2.89	1.15	Sp. No. In GREAVES
		M_2	1.91	1.14	44.973 et al. [1971]
		M_3	2.57	1.12	
	Fe^{3+}	(M_1, M_2, M_3)	0.57	0.40	
Cummingtonite	Fe^{2+}	(M_1, M_2, M_3)	2.72—2.90	1.14—1.18	BANCROFT et al. [1967]
		M_4	1.50—1.68	1.05—1.11	
Anthophyllite	Fe^{2+}	(M_1, M_2, M_3)	2.58—2.61	1.12—1.13	BANCROFT et al. [1967]
		M_4	1.80—1.81	1.09—1.11	
Crocidolite	Fe^{2+}	M_1	2.82	1.25	BANCROFT and BURNS
		M_3, M_2	2.39	1.25	[1969]
	Fe^{3+}	(M_1, M_2, M_3)	0.41	0.46	
Glaucophane	Fe^{2+}	M_1	2.82	1.22	BANCROFT and BURNS
		M_3, M_2	2.33	0.33	[1969]
	Fe^{3+}	(M_1, M_2, M_3)	0.48	0.45	

that the fraction f^* of Fe^{57} nuclei absorbing the γ-ray resonantly without recoil, to be the same for both Fe^{2+} and Fe^{3+} at M_1, M_2, M_3 sites.

It is presumed that Fe in Fe—Ti-oxide mineral inclusions have contributed counts only in the background part of the spectrum and significantly none in the peaks. Thus the Mössbauer analysis eliminates the Fe from minor oxide impurities whereas the chemical analysis (Table 1) might incorporate the unliberated magnetic fragments after crushing and magnetic separation. For comparison, hyperfine parameters of those reported from other amphiboles are presented in Table 3. It is seen that the I.S. of alkali amphiboles are generally above the value of 1.20 and larger compared to those of other amphiboles (Tables 2 and 3).

DISCUSSION

Kaersutites defined as titaniferous pargasite-ferropargasite series amphiboles have part of Mg replaced by Fe^{2+} and the general formula of type sample is shown as $(Na, K, Ca)_{2-3} (Mg, Fe^{2+})Ti\ Al_2^{IV}Si_6O_{23}(OH)$ by WILKINSON [1961]. Table 1 shows that Eifel kaersutite gives Si as 5.7 per formula unit having (O, OH, F)=24, which is slightly less than 6. Kaersutites from monzonite, teschenite and trachyte have Si content slightly higher than 6 and often have insufficient Al^{3+} to fill the Z group, while those crystallized in volcanic rocks have high Al^{3+} in the Z group.

* f' is defined as $\approx 1 - K^2 < \chi^2 >$ for an Einstein solid with $3N$ vibrational modes where N is, the number of atoms in the solid and $K = 2\pi/\lambda = E/\hbar c$, $< \chi^2 >$ is the component of mean square vibrational amplitude of the emitting nucleus in the direction of the gamma ray. It is therefore dependent on temperature and on the vibrational spectrum at each of the M sites.

[AOKI, 1963]. The Al^{3+} content (3.8 per formula unit) in the present sample is high and Al^{3+} fills up the Z group with Si^{4+} and one-third of the total Al^{3+} goes into Y group. This is higher than reported earlier from normal or oxidized kaersutites which have $Al \approx 2$ per formula unit *(ibid)*.

The high content of Al_2O_3 (3.87 — 10.84 wt.%) with Tschermak's component ranging from 5.9 to 18.4 mol. p.c. in clinopyroxenes in the wehrlite and clino-pyroxenite inclusions in the volcanics of Eifel region suggest the parent magmas to be alkali-basalt in composition and was located at relatively deep sites in the continental crust.

The calciferous amphiboles are supposed to have 1.8 to 2.1 Ca ions per formula unit [BOYD, 1959) and in this kaersutite having Ca to an amount of 2 show a pronounced substitution for Mg as common in calciferous amphiboles. (Na+K) of this sample is 0.9 with a ratio of 5:4 indicating fair availability of equivalent amount of these alkalies in the crsytallizing magma.

Crystallization of kaersutite-hornblende is presumed to be effected at high pressure temperature condition with hydrous environment. It is known that hornblende breaks down to garnet+ pyroxene at pressures above 12 Kb and temp. below 950 °C and brown hornblende is stable at total pressures of at least 13 Kb (corresponding to a depth of 40 km) at 900 °C when $P_{total} = P_{H_2O}$ [NISHIKAWA and KUSHIRO, 1967; LOVERING and WHITE, 1969]. At the same pressure and temp. conditions, it appears that amphibole crystallizes at an earlier stage of fractionation from a silica-undersaturated magma than from an oversaturated magma [AOKI, 1970]. Kaersutites of plutonic xenoliths from Tristan da Cuñha is supposed to have crystallized at water pressure below 1.4 Kb [LE MAITRE, 1969] i.e. below 5 km depth. Studies on the kaersutite-bearing inclusions in Iki Island, Japan by AOKI [1970] suggest that alkali-basalt magma crystallized phenocrysts of olivine, rare-aluminous orthopyroxene, aluminous clinopyroxene, kaersutite, plagioclase and titano-magnetite successively under hydrous conditions at depth of 25 to 30 km in the lowest part of the crust. On the basis of Al-content in the associated olivine-clinopyroxene nodules in the tuffs of Eifel, it may be presumed that identical high P—T hydrous condition must have controlled the crystallization of kaersutite below the crust in the Eifel region of W. Germany.

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DR. S. MITRA
Reader in Geology
Department of Geological Sciences
Jadavpur University
Calcutta-32, India