15597   VITROPHYRIC QUARTZ-NORMATIVE   ST. 9A   145.7 g
                 MARE BASALT

INTRODUCTION: 15597 is a fine-grained, pyroxene vitrophyric mare basalt with conspicuous small phenocrysts and vugs (Fig. 1). It is the most rapidly cooled of the larger samples of this basalt type and is widely believed to be unaffected by surface fractionation. Its chemistry is that of an average A15 quartz-normative basalt and has been used in crystallization experiments because it better represents a melt composition than other samples. The sample is medium dark gray, slabby with two flat faces, angular, and tough. It appears to be homogeneous, with yellow-green prismatic phenocrysts (weathering white) and a black groundmass. PET (Lunar Sample Information Catalog Apollo 15, 1972) recognized a lamination of some phenocrysts which has not been recognized in thin section. The vugs are small and about 1% of the total volume. Zap pits occur on most faces but are not dense.

15597 was collected in the vicinity of the boulder from which 15595 and 15596 were chipped, but has not been recognized in surface photographs. Its orientation is therefore unknown.

Figure 1. Macroscopic view of 15597. Sparse pigeonite phenocrysts and small vugs are visible. S-71-49940

PETROLOGY: 15597 consists of numerous, tiny pigeonite phenocrysts, commonly hollow, in a groundmass of opaque glass. Small vesicles are ubiquitous and pigeonite megacrysts are rare (Fig. 2). Published modes (Table 1) have high total phenocryst percentages. Drever et al. (1973) found no preferred orientation except an example of a radial arrangement of acicular phenocrysts. Donaldson et al. (1977) noted extreme discordancies in the sizes of phenocrysts and their uniform distribution indicating that they are not aggregations.

A comprehensive petrographic and microprobe study was given by Weigand (1972) and Weigand and Hollister (1973), with tabulated microprobe analyses. They noted that acicular pyroxene phenocrysts are 0.5 to 1.5 mm x 0.04 to 0.15 mm. Cross sections show prominent (100) faces and subordinate (010) faces. Simple twinning is common, parallel to (100). Phenocrysts commonly have a glass core, and some length sections exhibit a "swallow-tail." Both cores and the sharply bounded rims have extreme chemical zonation (Fig. 3) as also shown by the data of Grove and Bence (1977) and Drever et al. (1972) (also shown in Fig. 3). The first pyroxene to crystallize was $En_{70}Wo_4$, identified as pigeonite on low 2V values (less than 20°). The composition falls well within the range of lunar orthopyroxenes, and the pigeonite is probably metastable. This "inner" pigeonite zones out to about $En_{52}Wo_{15}$ ("outer" pigeonite), then is epitaxially grown with "inner" augite, $En_{40}Wo_{30}$, which is zoned extremely to $En_{10}Wo_{32}$ ("outer" augite). Minor sector-zoning was observed. Ti and Al are partitioned into inner augites relative to outer pigeonites (Fig. 3). Al_2O_3 and TiO_2 rise to extreme values at the augite rim (13.8% and 3.5% respectively), and Cr_2O_3 falls to very low abundances (~0.03%). A single large megacryst is remarkably homogeneous with only the outer 5% of the pigeonite zoned. Chemical evidence suggests however that it was not the first to nucleate and grow. Groundmass crystals are various skeletal ferroaugites with compositions similar to edges of augite rims. The pyroxene zoning patterns are explained by the crystallization of pyroxene in the absence of co-crystallizing plagioclase or Ti-rich minerals. Chromite is minor and has an irregular distribution. It has a bimodal size distribution. The larger (about 100 microns) are typically clustered, euhedral, and commonly partially enclosed in phenocrysts. The smaller (about 25 microns) are in phenocrysts or in groundmass. The chromites are Al-Mg-chromites grading into Ti-Mg-aluminian chromites (Fig. 4). In contact with glass matrix they are rimmed (1 to 2 microns) by ulvospinel. Weigand and Hollister (1973) tabulated chromite analyses and discussed the zoning trends. Nickel-iron grains are ubiquitous but of minor abundance. Ni varies from 4 to 7%, and Co from 1 to 3%: At least the large chromites appear to have completed crystallization prior to pyroxene nucleation, and metal grains to have at least nucleated before pyroxene nucleation. The glass groundmass of 15597 has an unusual composition (Table 2), with extremely low MgO. Gradients adjacent to crystals suggest that the rate of crystal growth exceeded diffusion rates in the melt. The overall sequence of crystallization for 15597 as inferred by Weigand and Hollister (1973) is shown in Figure 5.
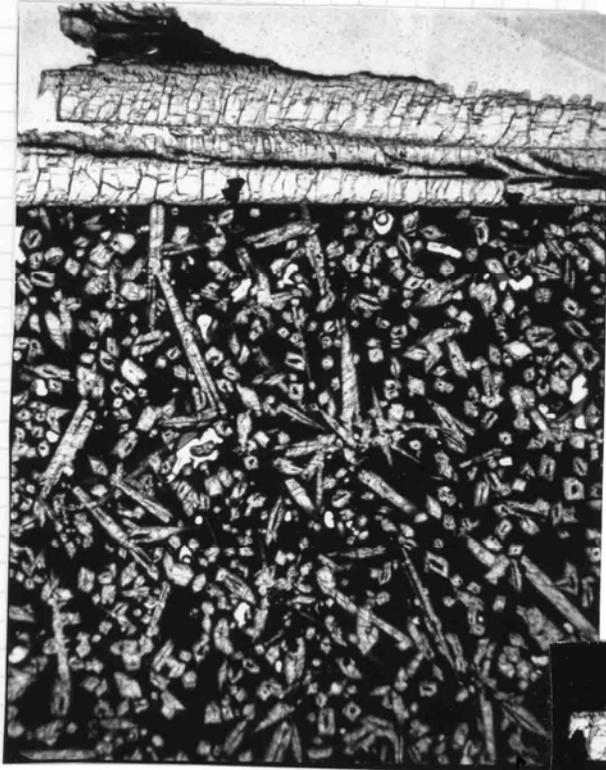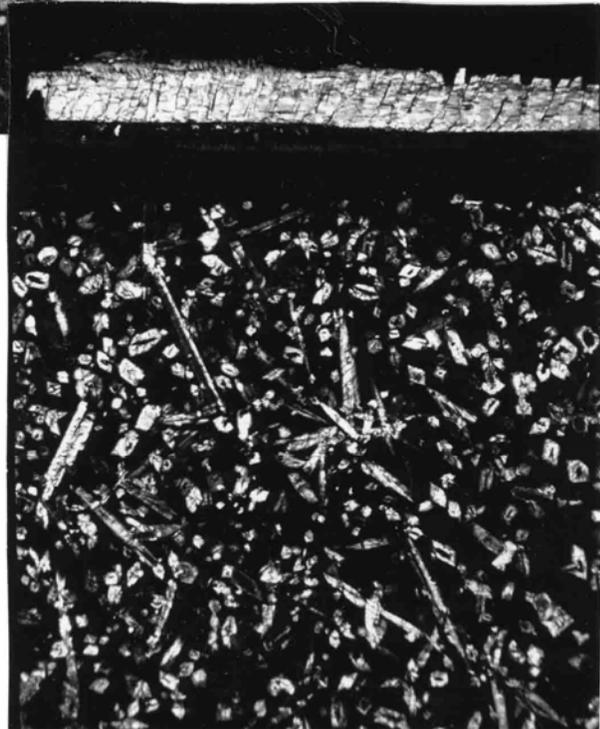
Figure 2. Photomicrographs of 15597,12,
showing small acicular phenocrysts, opaque glassy groundmass,
small vesicles, and part of a twinned megacryst
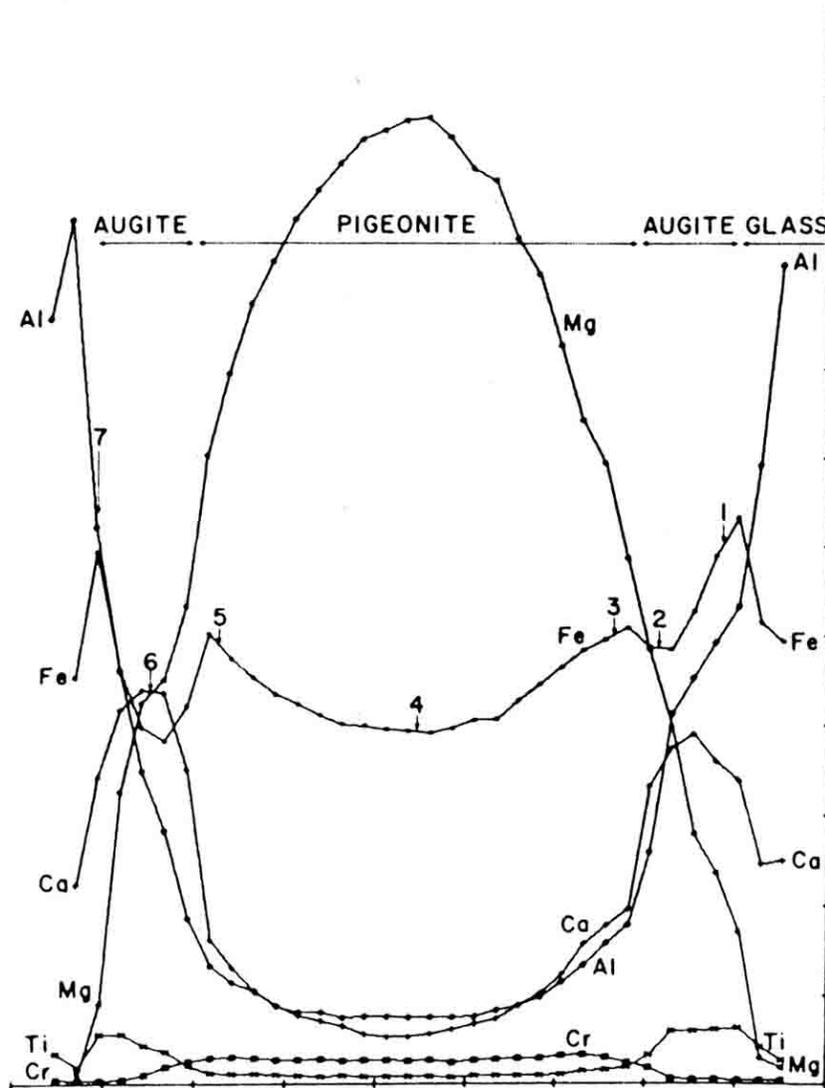, a) transmitted light; b) crossed polarizers.

Fig. 3a

Figure 3. Compositions of pyroxenes in 15597.
 a) typical elemental profile across a phenocryst. Vertical scale is raw
    intensity, analysis interval is 2 microns,
 b) compositional zoning in the quadrilateral. Triangle size is
    proportional to "others" components,
 c) Ti- Cr-Al trends,
 a)-c) from Weigand and Hollister (1973).
 d) sketch and analyses of radiate clinopyroxene (Drever et al., 1972).
 e) major and minor element analyses,
 f) minor element analyses of 15597 and other Apollo 15 quartz-
    normative basalt pigeonite cores, and experimental cooling rate
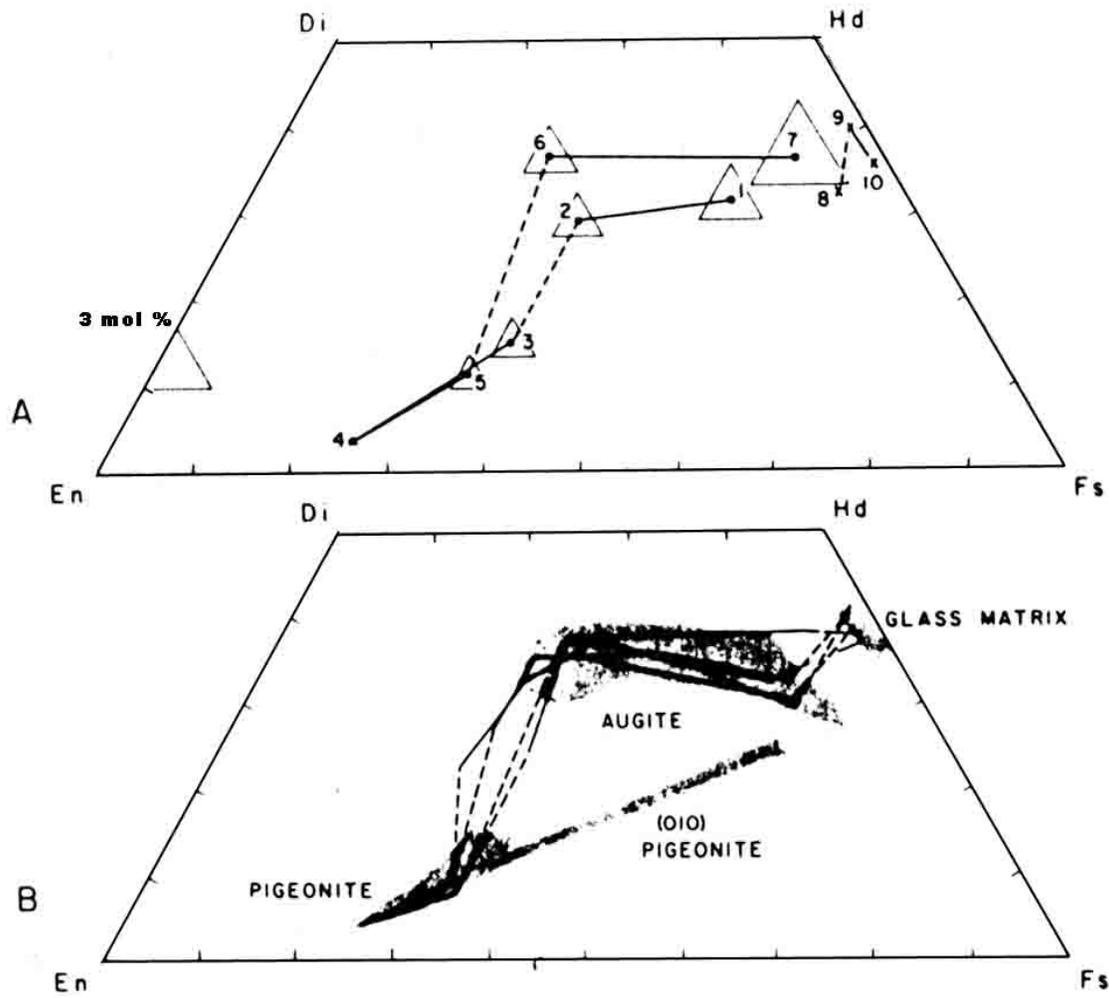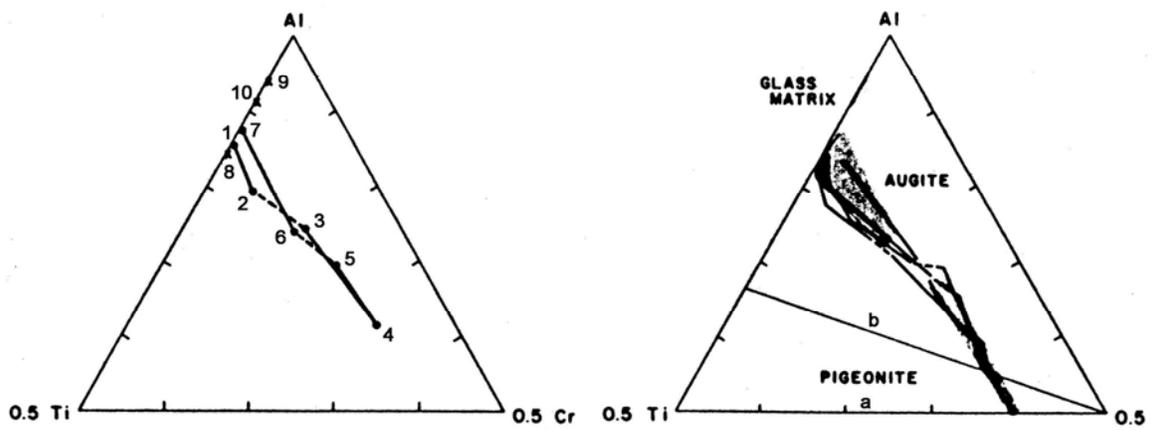   products,
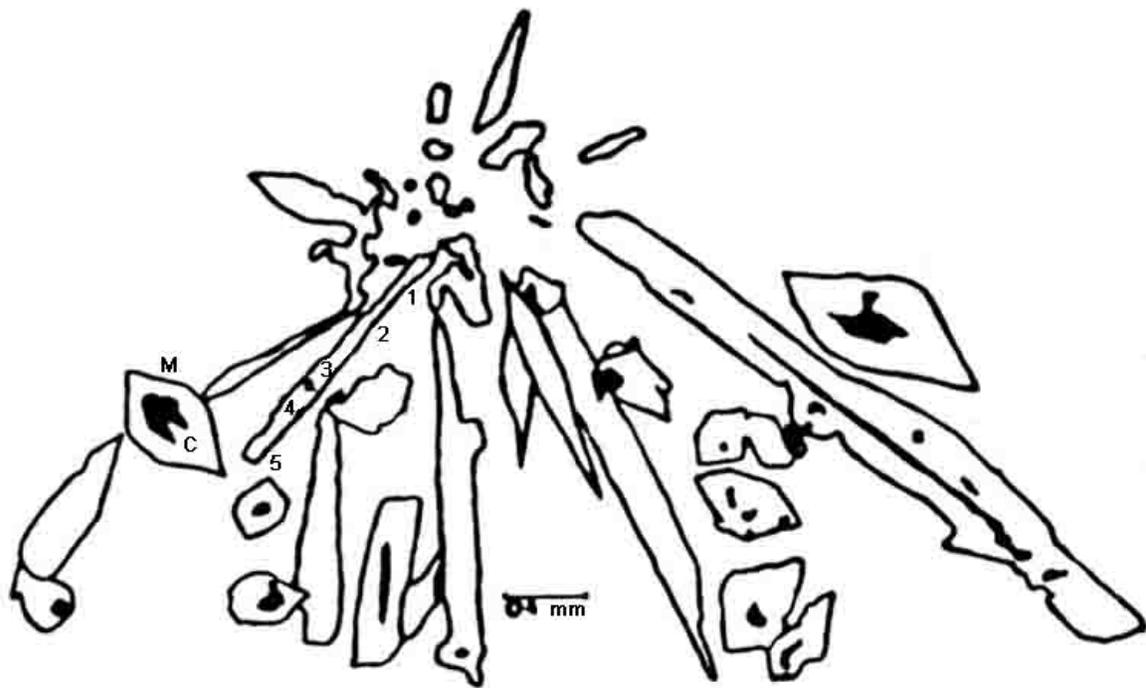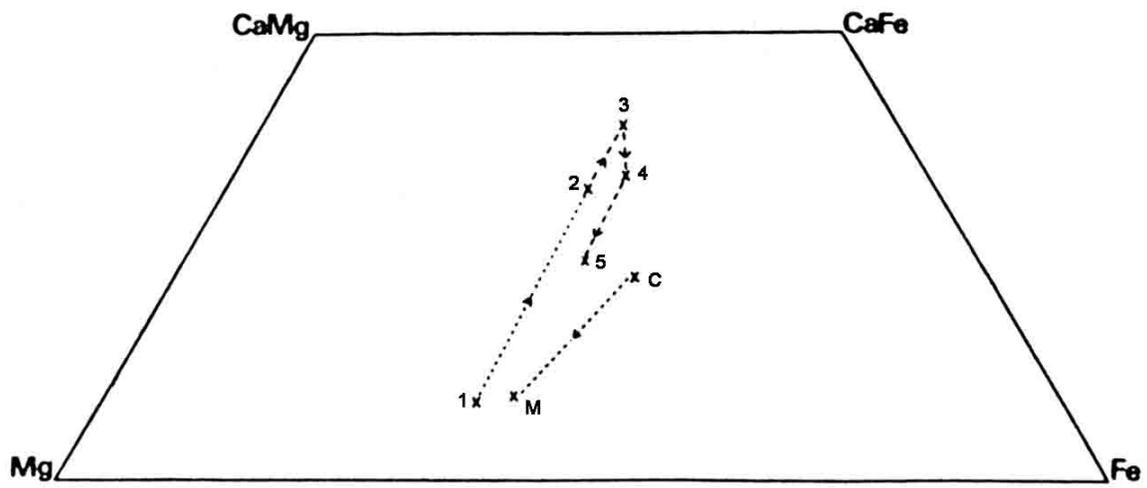 e) f) from Grove and Bence (1977).

Fig. 3b

Fig. 3c

CaMg   CaFe

3

2

4

5

C

1   M

Mg   Fe

M

C

1

2

3

4

5

0.4 mm

Fig. 3d

Fig. 3e

Fig. 3f

TABLE 15597-1. Modes of 15597

	(1)	(2)	(3)	(4)
Pig	42	59	55.8	50.1
Aug	17			
Glass	37	41	43.9	49.9
Opaques	<1	<0.3	0.3	<0.1
Vesicles	3	--	--	--

(1) Weigand and Hollister (1973)
(2) PET (Lunar Sample Information Catalog, 1972)
(3) Grove and Walker (1977)
(4) Papike et al. (1976)

TABLE 15597-2. Analysis of groundmass glass

		(1)	(2)
Wt %	SiO2	47.9	48.63
	TiO2	2.30	2.33
	Al2O3	15.13	16.05
	FeO	22.24	21.26
	MgO	1.40	0.43
	CaO	9.62	9.29
	Na2O	0.66	0.75
	K2O	0.111	0.13
	P2O5	0.151	0.14
ppm	Cr	<35	~70
	Mn	1740	~1500
	S	--	1600

(1) Nava (1974); AAS, colorimetry
(2) Weigand and Hollister (1973); microprobe

Figure 4. Cr-Al and Fe-Mg relationships in 15597 chromites.
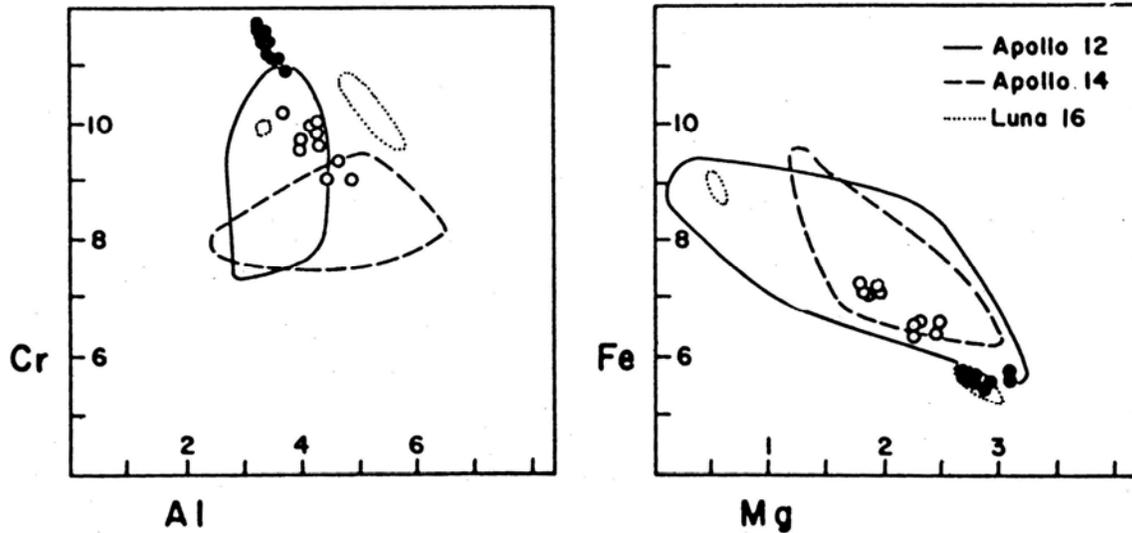Filled dots = large chromites, open dots = small chromites
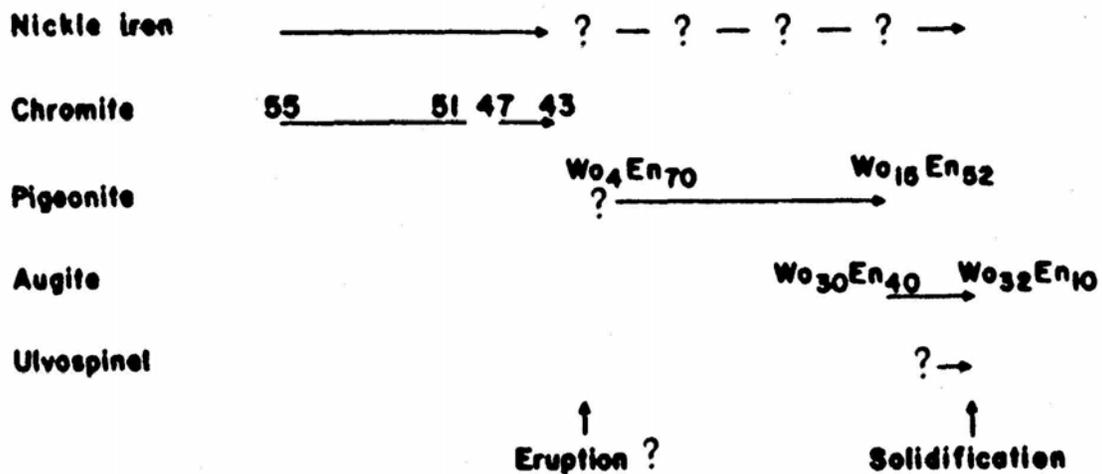(Weigand and Hollister, 1973).

Figure 5. Inferred crystallization sequence for 15597
(Weigand and Hollister, 1973). Numbers on chromite arrow are wt% Cr_2O_3.

Brown and Wechsler (1973) and Brown et al. (1973) used a precession camera, x-ray diffraction, and microprobe techniques to study pyroxenes. They found no augite exsolution (i.e., no (001) augite), suggesting very rapid crystallization from 1200°C to 950°C. Augite overgrows pigeonite epitaxially on (100). The pigeonite shows fine-scale polysynthetic twinning which could be from inversion from orthopyroxene (although no core orthopyroxene was observed, the compositions, $En_{70}Wo_4$, are well within the range of lunar orthopyroxenes). Coarse, simple growth twins are also not uncommon. Brown and Wechsler (1973) tabulated fractional atomic coordinates, bond lengths and angles, and other crystallographic data. There appear to be significant difference between class b peak diffusenes in 15597 and Mull pigeonites (contrary to the conclusion in Brown et al., 1973) indicating that 15597 cooled through the C→P transition (about 950°C) more slowly than the Mull pigeonite. The Fe-Mg distribution coefficient (Kd) of 0.12 for $En_{65}Wo_6$ is one of the most disordered reported and indicates equilibration at about 650°C. (The Brown et al., 1973, calculated Kd (0.18) is reported by Brown and Wechsler, 1973, as being in error.) Brown and Wechsler (1973) suggested that reheating could cause the discrepancy between the Fe-Mg equilibration temperature and the P→C phase transition, but the heating must not be enough to cause exsolution. However, in such reheating the groundmass glass might have devitrified. An alternative explanation is that reheating was a result of the heat of crystallization.

Cooling rate studies: Apart from the studies above, several experimental studies have been made to elucidate the cooling rate of 15597. Lofgren et al. (1974, 1975) found that the crystal morphologies and zoning trends of the phenocrysts resemble those produced in dynamic crystallization experiments with linear cooling rates of 5 to 20°C/hr. The groundmass is inferred similarly to have cooled at more than 30°C/hr. The groundmass is the most rapidly cooled of all those studied, but the phenocrysts (despite their smaller size and greater nucleation density) are inferred to have crystallized more slowly than those in vitrophyres 15485 and 15486. In a similar but more sophisticated study, Grove and Walker (1977) inferred an early cooling rate of 300° to 500°C/hr from the phenocryst nucleation density, an integrated rate of 10° to 150°C/hr from the pyroxene sizes, and a late-stage rate of 300° to 500°C/hr from plagioclase sizes. A megacryst was inferred to have grown during cooling at 3.75°C/hr. They inferred the final crystallizing position of 15597 from a conductive boundary to be 4 cm. They noted the variety of early stage cooling rates to be inferred, depending on which technique is used. They suggested that the megacrysts grew in a more slowly cooled environment for possibly a day or two. The nucleation density recorded by the smaller pyroxenes may have been biased by a concentration of nucleii during the event which increased the cooling rate.

Grove and Bence (1977) performed the experiments on which the Grove and Walker (1977) analysis is based. The summarized phase results are shown in Figure 6. They also used pyroxene compositions to assess cooling rates. The general zoning trends for 15597 are closest to these produced in 150°C/hr cooling rate experiments. The cores of phenocrysts have minor elements similar to these in much coarser rocks 15065 and 15058 (Fig. 3f) and most similar to those in 3.75°C/hr cooling rate experiments. Thus all these cores formed under similar conditions probably fairly close to equilibrium. The results confirm the complex cooling history and suggest nucleii formed in the interior of the

flow. Lofgren et al. (1979) performed experiments to compare the differing results of experiments on the 15597 composition which was used in the cooling rate studies. Grove (1982) used TEM techniques to study micro-exsolution textures in experimentally produces pyroxenes and in 15597, to assess cooling rates. Fine-scale tweed (001) and (100) modulations were found in 15597 with spinodal decomposition showing lamellar wavelengths of 165 and 170A (001) and being present on (100). Heterogeneous nucleation had a lamellar wavelength of 576Å (001) and absent on (100). The data indicate cooling at 20°C/hr, similar to but a littler slower than other estimations.

Other Experimental Studies: Muan et al. (1974, and quoted pers. comm. in Brown and Wechsler, 1973) conducted equilibrium crystallization experiments, in contact with metallic iron, on a powdered, representative piece of 15597. The liquidus phases were olivine and chromite at 1230°C, with pyroxene entry at 1170°C, and anorthite at 1140°C. The solidus was 1060°C. Grove and Bence (1977) reported similar equilibrium experiments in iron capsules in evacuated silica glass tubes with a realistic imposed fO_2. They had no iron loss from or gain to the charge. They found olivine (Fo_{68-70}) to be the liquidus phase, at 1215°C, and it reacted out by 1130°C (Fo_{56}). Pigeonite $En_{68}Wo_5$ entered at 1197°C and became more Ca, Fe-rich with decreasing temperatures. Spinel entered at 1185°C (a lower temperature than the Muan et al., 1974, experiments, a result of either higher chromium or higher oxidation state in the latter study). Plagioclase entered at 1143°C. Tabulated analyses of the run products were given.

Grove and Raudsapp (1978) conducted experiments on a 15597 synthetic composition to study the kinetic effects on pyroxene chemistry and the liquid line of descent, documenting the departures of dynamic liquid lines of descent from ideal fractional crystallization. Diffusion at the interface and the suppression of late phases during rapid cooling are important factors governing pyroxene and liquid chemistries. Residual liquids metastably penetrated the plagioclase primary phase volume.

Grove and Lindsley (1979a) conducted an experimental study on a late-stage liquid composition for 15597 at a cooling rate of 0.5°C/hr in an attempt to produce pyroxferroite and understand why pyroxferroite or alternatively fayalite and silica crystallize. If pyroxferroite was produced in the experiments, it was not as large or abundant as those in coarse-grained quartz-normative basalts, and the controlling factors for this (metastable) pyroxferroite production remain unknown. Grove and Lindsley (1979b) conducted experiments on synthetic compositions of 15597 and its residual liquids in a study of the partitioning of Fe, Mg, and Ca between pigeonite and liquids in basaltic liquids.

CHEMISTRY: Bulk rock chemical analyses are listed in Table 3 and the rare earths shown in Figure 7. The analyses are generally consistent, as might be expected of such a fine-grained, glassy rock, and are clearly of an average Apollo 15 quartz-normative basalt. It is a little lower in MgO and higher in FeO than some coarser members of the group, such as 15065. Helmke et al. (1973) placed 15597 in a low Sm/Eu group of quartz-normative mare basalts. Compston et al. (1972) noted that their Rb determinations by XRF were systematically lower than their more reliable isotope dilution analyses.
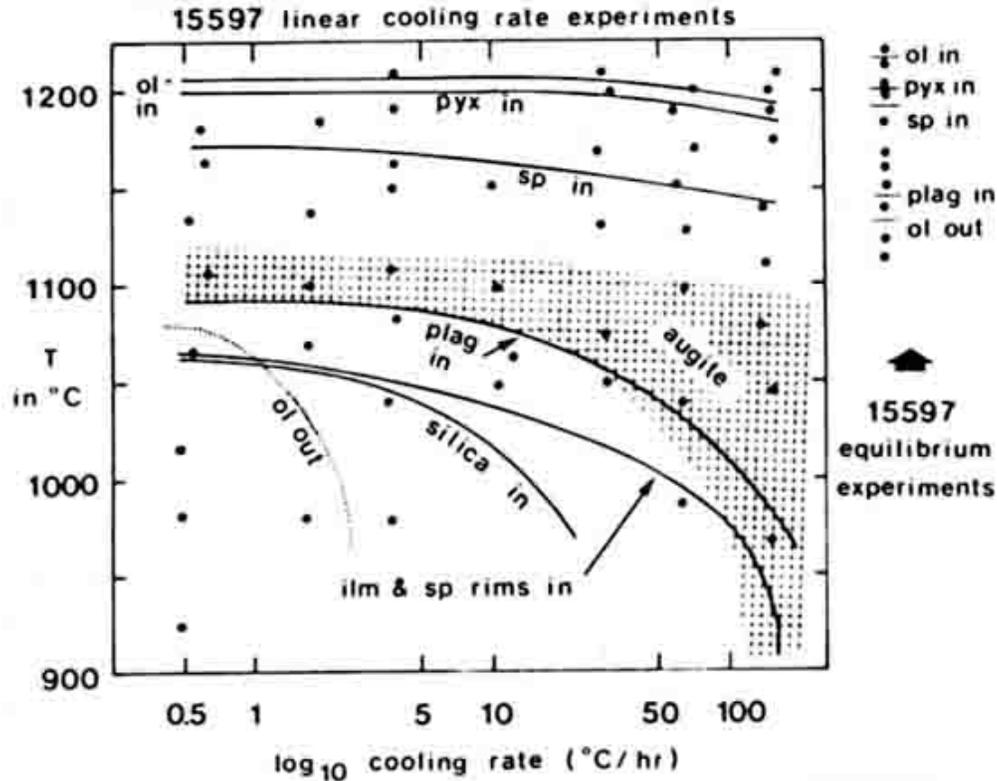
Figure 6. Summary of linear controlled cooling rate
and equilibrium experiments on synthetic glass
with the bulk composition of 15597 (Grove and Bence, 1977).

Nava (1974) reported an analysis of the groundmass glass separated from ground bulk rock powder by heavy liquid methods.

STABLE ISOTOPES: Clayton et al. (1972) reported $\delta^{18}O$ values of 5.60 for glass and 5.41 for pigeonite, without specific discussion. They are typical lunar values.

RADIOGENIC ISOTOPES AND GEOCHRONOLOGY: Kirsten et al. (1973)reported a ^{40}Ar-^{39}Ar plateau age of between 3.1 and 3.5 b.y., an imprecise age but covering the known age of other Apollo 15 quartz-normative mare basalts. The sample contains large amounts of excess argon, released between 580°C and 880°C, which Kirsten et al. (1973) suggest was probably incorporated while the magma was upwelling through older crust and then frozen in.

Compston et al. (1972) reported Rb-Sr isotopic data for a whole rock sample. The $^{87}Rb/^{86}Sr$ (0.0294) and $^{87}Sr/^{86}Sr$ (0.70091 ± 10) give an initial $^{87}Sr/^{86}Sr$ of 0.69953 for an assumed age of3.35 b.y., an initial value indistinguishable from other Apollo15 mare basalts.

TABLE 15597-3. Bulk rock chemical analyses

		,21	,8	,19	,0	,21	,27	,6
wt %	SiO2	47.98	48.0	48.1				
	TiO2	1.80	1.84	1.87				
	Al2O3	9.44	9.55	9.27				
	FeO	20.23	20.6	20.17				
	MgO	8.74	9.06	9.18				
	CaO	10.43	10.4	9.69			9.5	
	Na2O	0.32	0.317	0.32				
	K2O	0.06	0.078	0.056	0.053		0.053	
	P2O5	0.07		0.107				
(ppm)	Sc							
	V							
	Cr	3290		3356				
	Mn	2320	2160	1970				40
	Co							
	Ni		30					
	Rb	0.90				1.13		0.72
	Sr	109.4	91			111.0		
	Y	27						
	Zr	101						
	Nb	6						
	Hf							
	Ba		52					
	Th				0.53			
	U				0.14			
	Pb							
	La		4.86					
	Ce		13.0					
	Pr							
	Nd		9.3					
	Sm		3.09					
	Eu		0.84					
	Gd		4.4					
	Tb		0.69					
	Dy		4.51					
	Ho		0.86					
	Er		1.9					
	Tm							
	Yb		2.13					
	Lu		0.301					
	Li							
	Be							
	B							
	C							
	N							
	S	600						
	F							
	Cl							0.024
	Br							
	Cu							1.2
	Zn							
(ppb)	I							
	At							
	Ga	2600						
	Ge							
	As							117
	Se							
	Mo							
	Tc							
	Ru							
	Rh							
	Pd							0.90
	Ag							1.7
	Cd							0.59
	In							
	Sn							1.49(a)
	Sb							1.9
	Te							37
	Cs							
	Ta							
	W							
	Re							.0081
	Os							.0072
	Ir							
	Pt							
	Au							.045
	Hg							0.32
	Tl							0.21
	Bi							
		(1)	(2)	(3)	(4)	(5)	(6)	(7)

References for Table 15597-3

References and methods:

(1) Chappell and Green (1973), Compston et al. (1972); XRF
(2) Helmke et al. (1973); INAA, AAS, RNAA
(3) Nava (1974); semi-micro, AAS, colorimetry
(4) O'Kelley et al. (1972); gamma ray spec
(5) Compston et al. (1972); ID/MS
(6) Kirsten et al. (1973); argon, irradiation
(7) Ganapathy et al. (1973); RNAA

Notes:

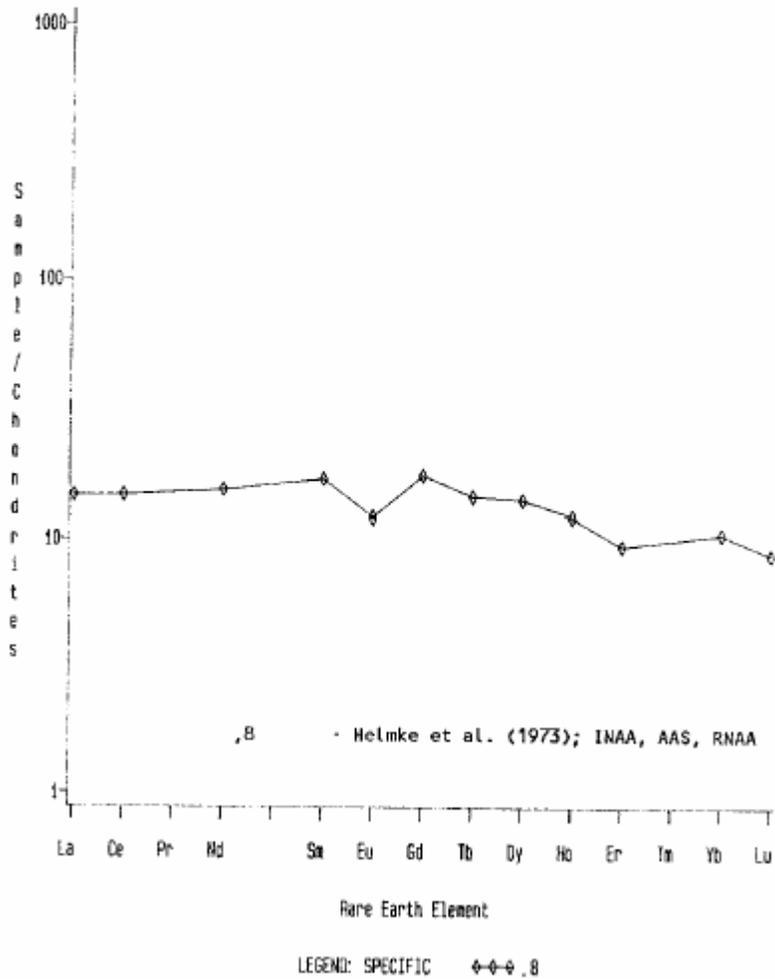(a) doubtful -- contamination or analytical error--in authors' own judgement.

Figure 7. Rare earths in 15597.

RARE GASES, RADIONUCLIDES AND EXPOSURE: Kirsten et al. (1973) reported a [38]Ar exposure age of 210 m.y., without comment. Eldridge et al. (1972) reported disintegration count data for [22]Na, [26]Al, and [54]Mn without discussion. The [26]Al is saturated (Yokoyama et al., 1974) indicating exposure of a million years or more.

PHYSICAL PROPERTIES: Hargraves and Dorety (1972) measured the intensity of the natural remanent magnetization, saturated IRM, and their variation with AF demagnetization (Fig. 8). They found that their sample had a stronger intensity of remanence than many of the other samples they analyzed, even higher than the older Apollo 11 basalts. Fuller et al. (1979) made a comprehensive study of the magnetism of 15597 and some other fine-grained basalts. They found that two subsamples of ,20, whose mutual orientations are not known, gave different AF demagnetization curves but that both had good directional stability (Fig. 9). Thermal demagnetization to 100°C had no significant effect on the NRM. The magnitude of the NRM in the two subsamples differed by almost an order of magnitude. The stability of the NRM is less than the anhysteric remanent magnetization (ARM) and saturated IRM, so is unlikely to be a thermoremanent magnetization; the NRM was acquired by a single process which activated hard and soft microscopic coercivities. Fuller et al. (1979) believed that the NRM was too soft to be of thermal origin and too hard to be simply isothermal contamination. The explanation they considered to be least unacceptable was that the NRM was a shock remanent magnetization. Paleointensity field derivations hence must be virtually impossible. Fuller et al. (1979) also tabulated many of the magnetic properties derived from hysteresis loops. The saturated magnetization (Js) and the Jr/Js are so small that a mixture of single domain with either multidomain or super-paramagnetic grains is suggested. Heating experiments showed little change in the saturated magnetization but the saturated IRM increased by an order of magnitude.

Cisowski et al. (1983) (of which Fuller is a co-author) contested the NRM data of Hargraves and Dorety (1972), suggesting that the chip used was small and its high NRM was magnetically contaminated.   Cisowski et al. (1983) made new measurements and, with the data from Fuller et al. (1979) noted that the NRM's were an order of magnitude lower. In contrast with Fuller et al. (1979), Cisowski et al. (1983) believed that paleointensity data were obtainable and that the NRM was not a shock remanent magnetization.

PROCESSING AND SUBDIVISIONS: A single, nearly 20 g piece (,1) was chipped from the "W" end and entirely subdivided for the initial allocations. Subsamples included ,7, made into a potted butt and partly used to make thin sections ,7; ,16; ,18; and ,23; potted butt ,22 (thin sections ,24 to ,26); thin sections were also made from pieces of ,2 (thin sections ,11; ,12; ,14; ,15; and ,17). Further chippings were made from the same area to fulfill chemistry allocations, and, in 1979, magnetism allocations.
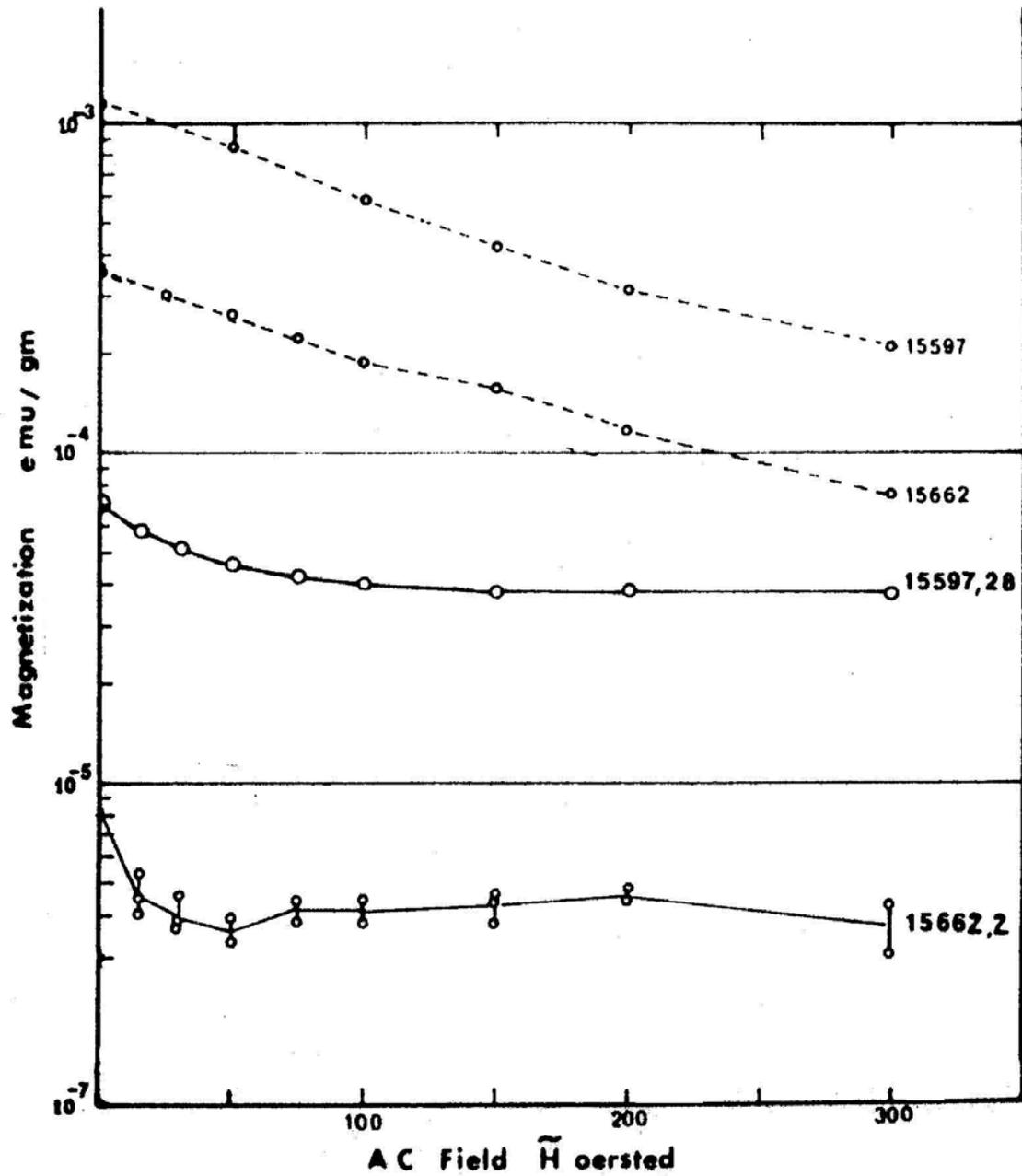
Figure 8. NRM intensity (solid line) and saturated IRM (dashed line) for 15597 and 15662 (Apollo 15 olivine-normative mare basalt). (Hargraves and Dorety, 1972).
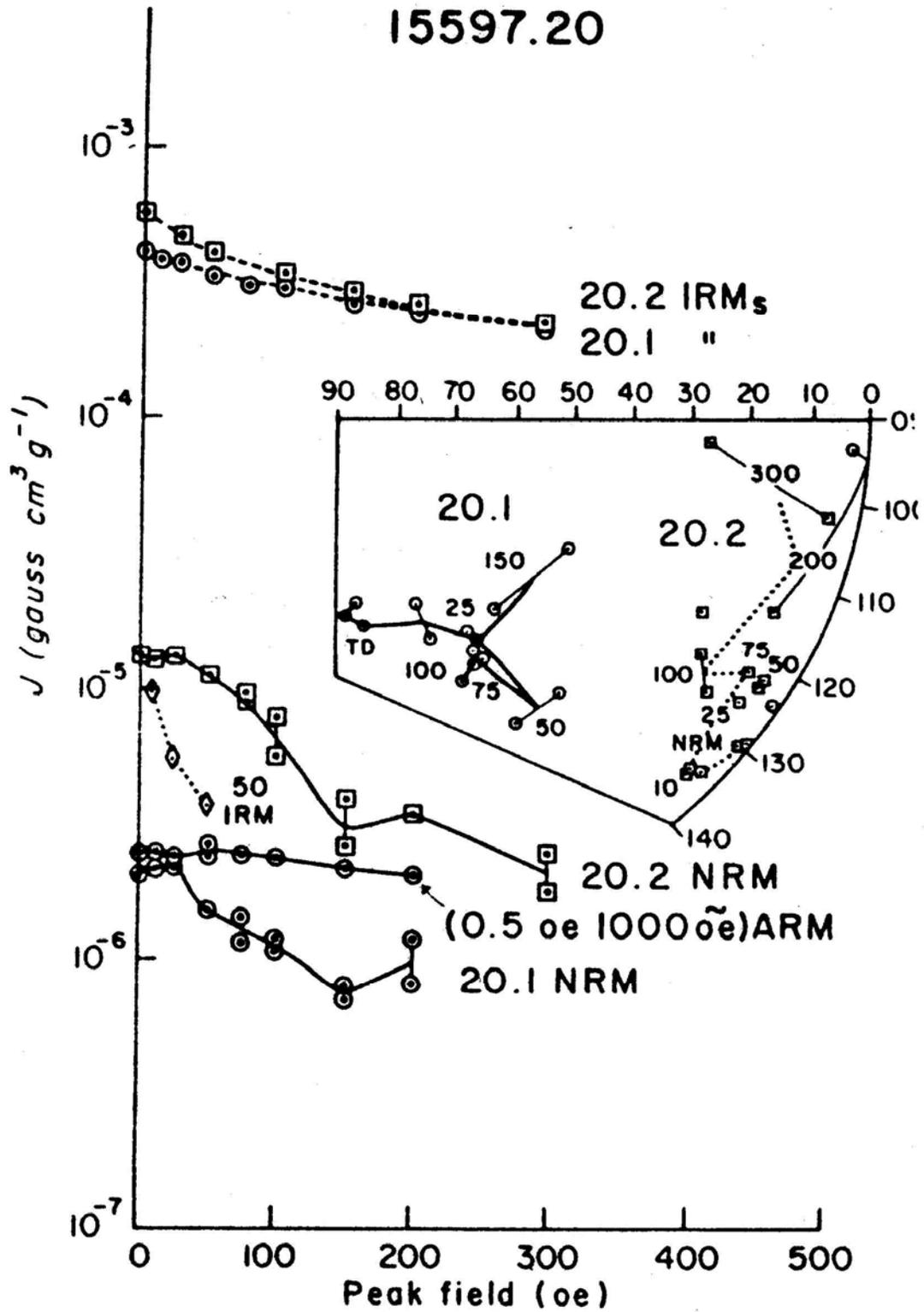
15597.20

Figure 9. AF demagnetization of 15597,20.
Inset is directional changes. (Fuller et al., 1979).