Iron in the Minerals of the Sodalite Group

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Abstract. The study of the problem of the black coloration of feldspathoids of the sodalitic group (nosean, haüyne, sodalite) reveals iron as a main factor.
A statistical study of the global compositions of these minerals proves that their enriching in Fe is accompanied by a decrease in Al, but also by an increase in Si.
A substitution of Fe^{+++} to Al in the structure in the feldspathoids is suggested.
The analysis with an electron microprobe confirms this hypothesis and allows us to state a fondamental difference between the formation of miaskitic phonolites rich in Fe^{++} and that of agpaitic phonolites rich in Fe^{+++}.

In France under-saturated alcaline rocks of the phonolite type can hold nepheline (Lacroix, 1891); yet, usually, they hold minerals of the sodalitic family. Nosean-haüyne and sodalite are then mixed, or unmixed with analcime (Brousse, 1959; Vatin-Pérignon, 1966; Varet, 1967). The presence of sodalitic minerals is not restricted to alcaline phonolites only, but it is also constant in subalcaline phono-lites and tephrites (ordanchites) of the Massif of the Mont-Dore, of the Cantal and of the Velay, as well as their authigenous inclusions (Haüynite-gabbro or Mareugites). More exceptionally (we found one instance only, St. Micaud in the Charolais) they can be met in a picrite-basanite (Brousse and Nativel, 1963). We know that the members of the nosean-haüyne series are usually of a bluish colour, whereas the sodalite is colourless; but many of them have a black colora-tion which is sometimes so intense that grains appear as opaque bodies. In other cases, it is simply a grey pigmentation, with the grains scattered among the body of the feldspathoid.

Our attention is drawn at once to the variability in the aspect of the sodalitic minerals; this variability is marked at the same time by differences in the colour of this or that cristal and also by differences in the colour shared in zones of the same section. Among the frequent cases, let us also note the minerals in which one zone only is black, usually on the brim (Fig. 1).

We have used two different methods so as to grasp the reasons of those colour-variations. Whenever possible, we have isolated the generations of grains of a different colour so as to get to a global chemical analysis (3g of minerals were separated in each sample); and, secondly, we made analyses with an electron microprobe. Let us note that the minerals of the *nosean-haüyne* group, which form a complete solid solution above 600°C and PH_2O of 1000 bars (Van Peteghem and Burley, 1963), in the following range. $(Na_{5-8} \ K_{0-1} \ Ca_{0-2} \ \square_{0-1})_8$ $(Al_6 \ Si_6 \ O_{24}) \ (SO_4)_{1-2} \cdot n \ H_2O$, were determined thanks to the position of

0   100μ

0   100μ
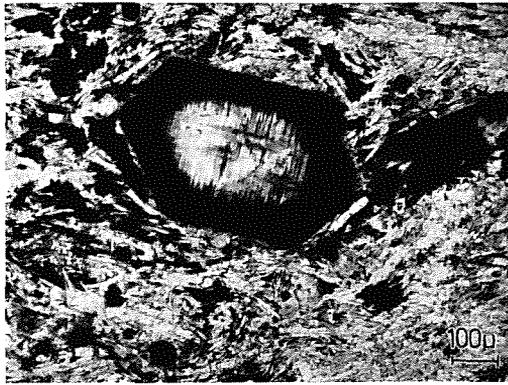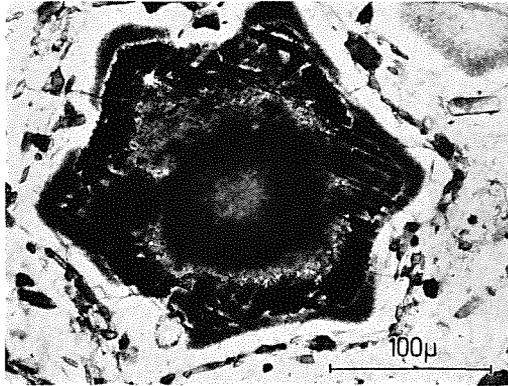
Fig. 1. Micrograph of colourless black-rimmed *sodalite* of the agpaitic phonolite of Auteroche and section (111) in "fort Vauban" of a *nosean* taken in the miaskitic phonolite of Vinsac

their most intense line (211) at 3.72 ± 0.01 Å while using the quartz line (101) as an internal standard (VAN PETEGHEM and BURLEY, 1962). The identification of the sodic nosean, of the more calcic haüyne was then made by measuring their refractive index (BROUSSE, 1961, p. 138); the index of the noseans and haüynes are respectively inferior or superior to 1.493. Only in a few rare cases we could use the criterion proposed by TAYLOR (1967): the line (100) at $d = 9.127$ Å allows him to mark the distinctive line between the noseans (the stripe is present in P$\bar{4}$ 3m) and the haüynes (the reflection is missing in P$\bar{4}$ 3n). Indeed, the line (100) has only an intensity of 10 at the most, compared to the intensity 100 of the line (211) and consequently it is difficult to recognize it on the powder diagrams.

As for *sodalite*, we know it can contain 10% of either nosean or haüyne in a solid solution as soon as temperature reaches 600° C and pH$_2$O 600 bars (VAN PETEGHEM and BURLEY, 1963); we have identified it by marking the position of the main reflection (211) at 3.62±0.01 Å. We checked this determination by measuring the refractive index at 1.485±0.001 and also by marking its reactions in a thermo-analysis. Indeed, nosean and haüyne have a H$_2$O content ranging from 0.40% to 4.60% (TAYLOR, 1967); so it is probably zeolitic water (TAYLOR, 1968) since the
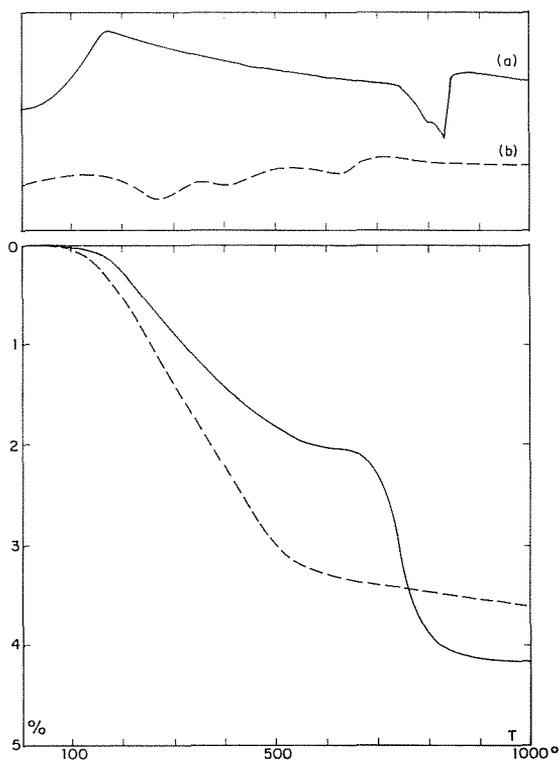
Fig. 2. Curves of thermodifferential (above) and thermoponderal (below), curves of the sodalite of Cournil (*full line*) and of the nosean of Vinsac (*dotted line*). Heating-speed of 600°C/h for the thermodifferential analyses and of 300°C/h for the thermoponderal analyses

progressive departure (from 100 to 600°C) is easy because there are no endo- nor exothermal reactions; moreover, the final product keeps the characteristics of the original nosean-haüyne (Fig. 2). As for the natural sodalites, Na_8 $(Al_6$ Si_6 $O_{24})$ $Cl_2 \cdot n$ H_2O, they should have (TAYLOR, 1967) 0.60 to 1.20% water ($n = 0.4$ — 0.6); these grades seem clearly lower to those of the artificial sodalites, M_8 $(Al_6Si_6O_{24})$ $(OH)_2 \cdot nH_2O$, for which the water contents are $n = 3.02 - 2.74 - 3.30$ (BARRER and FALCONER, 1956) for M = Na, Ag and Li respectively. Yet a progressive departure of zeolitic water appeared (Fig. 2) between 150 and 700°C from 1 to 2%; but there also exists another departure of about 2% between 750 and 850°C. In a differential thermo-analysis, the first departure corresponds to an exothermal pike whereas the second corresponds to an endothermal reaction. All in all, the behaviour of sodalites and nosean-haüynes in thermo-analysis is different, at least as far as the samples we studied are concerned.

I. Occurrence of the Analysed Minerals

Among the rocks of the differentiated, under-saturated series (JUNG and BROUSSE, 1962), ranging from alkali-basalts rich in olivine to phonolites, we have only studied hololeuco-phonolites (Table 1).

It will be noted that we are isolating two petrogenetical types (BROUSSE, 1963, VARET, 1968) in this group of alcaline rocks. The first is that of the miaskitic phonolites, or phonolites made nearly exclusively of the normative minerals

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Table 1. *Paragenesis of the feldspathoids of the Auvergne lavas*

Rocks	Minerals			
	Phenocrystals		Groundmass	
	Haüyne	Nosean	Sodalite	Analcime
Ordanchite	x			x
Leuco-phonolites	x		ε	x
Hololeuco-phonolites				
Miaskitic		x	x	ε
Agpaitic		ε	x	x

x = present, ε = trace of.

Table 2. *Analyses of the Auvergne feldspathoids*

	1	2	3	4	5	6
SiO_2	35.75	35.44	35.94	34.26	35.84	29.49
Al_2O_3	28.20	24.99	23.94	28.03	22.67	23.95
Fe_2O_3	—	2.74	2.79	1.36	2.10	1.23
FeO	—	0.09	0.04	—	0.00	0.11
MnO	—	0.01	0.01	0.01	0.00	0.01
MgO	—	0.92	0.39	—	0.14	0.00
CaO	3.12	3.60	3.43	4.71	4.79	9.27
Na_2O	20.70	16.62	16.56	23.52	20.88	15.75
K_2O	0.62	1.97	2.59	1.40	1.06	1.94
TiO_2	—	0.03	0.03	—	—	0.40
P_2O_5	—	0.08	0.03	—	—	0.20
Cl	0.40	1.56	1.34	1.43	6.42	0.30
SO_3	7.36	8.77	8.79	3.78	2.35	13.38
H_2O^+	{ 3.20	2.04	4.24	0.98	2.01	2.01
H_2O^-		1.00	0.34	0.49	0.85	1.75
	99.35	99.86	100.46	99.97	99.11	98.75
$O \equiv Cl$	0.09	0.35	0.30	0.32	1.44	0.08
Total	99.26	99.51	100.16	99.65	97.67	98.67

In column A, numbers of ions on the basis of 21(O), associated to $6\ SiO_2 \cdot 3(Al,\ Fe^{3+},Ti)_2\ O_3$.

	1		2		3	
	A	B	A	B	A	B
Si	6.19 ⎫	6.22 ⎫	6.30 ⎫	6.36 ⎫	6.43 ⎫	6.51 ⎫
Al	5.75 ⎬ 11.94	5.78 ⎬ 12.00	5.23 ⎬ 11.90	5.27 ⎬ 12.00	5.04 ⎬ 11.85	5.11 ⎬ 12.00
Fe^{+++}	— ⎭	— ⎭	0.37 ⎭	0.37 ⎭	0.38 ⎭	0.38 ⎭
Ti	—	—	—	—	—	—
Fe^{++}	— ⎫	— ⎫	0.01 ⎫	0.01 ⎫	0.01 ⎫	0.01 ⎫
Mg	—	—	0.24	0.25	0.10	0.01
Ca	0.58 ⎬ 7.66	0.59 ⎬ 7.71	0.69 ⎬ 7.11	0.69 ⎬ 7.17	0.66 ⎬ 7.14	0.67 ⎬ 7.10
Na	6.94	6.98	5.72	5.77	5.79	5.81
K	0.14 ⎭	0.14 ⎭	0.45 ⎭	0.45 ⎭	0.59 ⎭	0.60 ⎭
Cl	0.01 ⎫ 0.97	0.01 ⎫ 0.98	0.47 ⎫ 1.64	0.47 ⎫ 1.65	0.41 ⎫ 1.59	0.42 ⎫ 1.61
SO_4	0.96 ⎭	0.97 ⎭	1.17 ⎭	1.18 ⎭	1.18 ⎭	1.19 ⎭
OH	—	—	1.18	1.19	0.40	0.40

Or + Ab + Ne. The last composition, that of the eutectoical R, from the experimental diagram (BOWEN, 1937, SCHAIRER, 1950), is Si 52.2; Al 23.9; K 6.7; Na 17.2. The primary mineral in those rocks is alcaline fedspath (anorthose $Or_{55-70}Ab_{50-30}An_{2-5}$), to which must be added a few rare coloured minerals, such as aegyrine — augite, kaersutite, zircon, and sphene. The sodalitic feldspathoid appears *after* the minerals Ca — Fe — Mg, but before anorthose. Analcime and calcite mark the end of the history of these rocks.

As for the *agpaitic phonolites*, they have a rate in agpaicity (ZLOBIN, 1959) (Na) = $\dfrac{Na}{Al-K}$, superior to 1,2; similarly, their index (Na′) = $\dfrac{Na+K}{Al + Fe^{3+} + Ti}$ (GERASSIMOV-SKY, 1956) comes near to 1.3. According to the norm, aegyrine and metasilicate of sodium are added to feldspatho-feldspathoidic minerals. The order of crystallisation of these rocks agrees with that of experimental mixtures, Ab — Ac — Ne — Di. There is a succession in the order of anorthose — sodalite — aegyrine — mosandrite and analcime.

It is important to note the position of the feldspathoids here, for in the miaskitic phonolites, they succeed to the ferromagnesian minerals; whereas in the agpaitic phonolites, rich in Fe^{3+}, they come before the formation of aegyrine.

1 = Phenocrystal of nosean of the miaskitic phonolite of Vinsac (Cantal), according to A. LACROIX (1901).

2 = Phenocrystal of nosean of the miaskitic phonolite of Vinsac (Cantal), according to J. VARET (1967).

3 = Phenocrystal of nosean of the miaskitic phonolite of Aldis (Cantal), according to J. VARET (1967).

4 = Holofeldspathoidic inclusion of sodalite-nosean in the agpaïtic phonolite of Cournil (Cantal), according to F. TALBOT (unpublished).

5 = Sodalite inclusion in the agpaïtic phonolite of Cournil (Cantal) according to J. VARET (1968).

6 = Haüyne crystal, in the mareugite of Suc du Lac (Cantal), in R. BROUSSE and R. MAURY (to be published).

In column B, number of ions on the basis of $\sum (Si + Al + Fe^{3+} + Ti) = 12$

4		5		6	
A	B	A	B	A	B
5.60 ⎫ 5.39 ⎬ 11.16 0.17 ⎭ —	6.02 ⎫ 5.80 ⎬ 12.00 0.18 ⎭ —	6.60 ⎫ 4.91 ⎬ 11.80 0.29 ⎭ —	6.71 ⎫ 4.99 ⎬ 12.00 0.30 ⎭ —	6.02 ⎫ 5.75 ⎬ 12.02 0.19 ⎭ 0.06	6.01 ⎫ 5.74 ⎬ 12.00 0.19 ⎭ 0.06
— ⎫ — ⎪ 0.82 ⎬ 8.55 7.44 ⎪ 0.29 ⎭	— ⎫ — ⎪ 0.89 ⎬ 9.20 8.00 ⎪ 0.31 ⎭	— ⎫ 0.04 ⎪ 0.94 ⎬ 8.67 7.44 ⎪ 0.25 ⎭	— ⎫ 0.04 ⎪ 0.96 ⎬ 8.84 7.57 ⎪ 0.27 ⎭	0.02 ⎫ — ⎪ 2.03 ⎬ 8.78 6.22 ⎪ 0.51 ⎭	0.02 ⎫ — ⎪ 2.03 ⎬ 8.77 6.21 ⎪ 0.51 ⎭
0.40 ⎫ 0.46 ⎬ 0.86 0.53	0.43 ⎫ 0.50 ⎬ 0.93 0.57	1.99 ⎫ 0.26 ⎬ 2.25 1.04	2.02 ⎫ 0.33 ⎬ 2.35 1.06	0.10 ⎫ 1.90 ⎬ 2.00 2.38	0.10 ⎫ 1.90 ⎬ 2.00 2.38

II. Global Chemical Analyses

In Table 2 will be found the 6 analyses of nosean-haüyne, made from the minerals in Auvergne. The structural formula has been calculated either on the basis of 6 SiO_2, 3 (Al, Fe^{3+}, Ti)$_2$ O_3 (Deer *et al.*, 1962), or on that of (Si + Al + Fe^{3+} + Ti) = 12 (Brousse, 1961). Yet, in both cases we have considered the *a priori* hypothesis that Fe^{3+} is substituted to Si or to Al in the tetrahedrons of the structure. This hypothesis, however likely, and similar to that made for the ferriferous alkali-feldspaths (Coombs, 1954; Carmichael, 1965), does not actually allow us to be sure about the substitution of (Si, Al) by Fe^{3+} without electron paramagnetic resonance investigation (Marfunin *et al.*, 1967). Indeed, this is due to the fact it is not possible to deduce the structural formulas of the sodalitic minerals by looking for the cations associated to a given number of ions O.

We have avoided this difficulty by establishing the correlations between Fe^{3+} and the tetrahedrical ions Al^{3+} and Si^{4+}; we have used here the mineral analyses of Taylor (1967) and Brousse (1961).

In Fig. 3, in which the values of Al_2O_3 and of SiO_2 are shown in relation to Fe_2O_3, it will be noticed that there is indeed a correlation between these different oxides. Not only does *the quantity of* Al_2O_3 *decreases as* Fe_2O_3 *increases* but the departure of more that one molecule of Al_2O_3 corresponds only to the addition of one molecule of Fe_2O_3. If there was simply a replacement of Al by Fe^{3+}, the equation of the line of regression would be $Al_2O_3 = -\frac{102}{80}$ $(Fe_2O_3) + 30.3$, (or, $Al_2O_3 = -1.275$ (Fe_2O_3) + 30.3); whereas it is in fact $Al_2O_3 = -2.17$ $(Fe_2O_3) + 30.3$.

This means that the arrival of Fe_2O_3 also corresponds with an increase, in nosean haüynes, in SiO_2.

All in all, *when Al decreases it seems to be replaced at the same time by* Si_4^+ *and by* Fe^{3+}. These datas show the considerable importance of iron and explain its majorole in the structure of sodalitic minerals and most probably in the tetrahedron structure.

III. Electron Microprobe Analysis

1. Theoretical Conditions of Measure

Bear in mind first of all that under the effect of electronic bombardment the minerals get hot, the maximum Θ_m temperature of a target being (Castaing, 1952, p. 28) $\Theta_m = \frac{3 W_0}{4 \pi J C r_0}$ where W_0 is the power received by the half-sphere of r_0 radius placed under an uniformly spread incidental energy (r_0 is of the same range as the radius of the probe).

Three kinds of behaviour of the minerals can be noted here: a) Some minerals (metallic oxides, nesosilicates, pyroxenes) seem to undergo no kind of damage and the study surface remains unaltered except for the point of impact where a contamination spot appears, due to a local destruction of the oil vapours always present on the sample and inside the microprobe.

In these cases favourable for a chemical analysis since the mineral material remains unchanged, part of the thermal flow is drained through the metallic film. b) In other cases, a temperature gradient is established from the point of impact and motivates a selective diffusion of the elements of the crystalline framework.
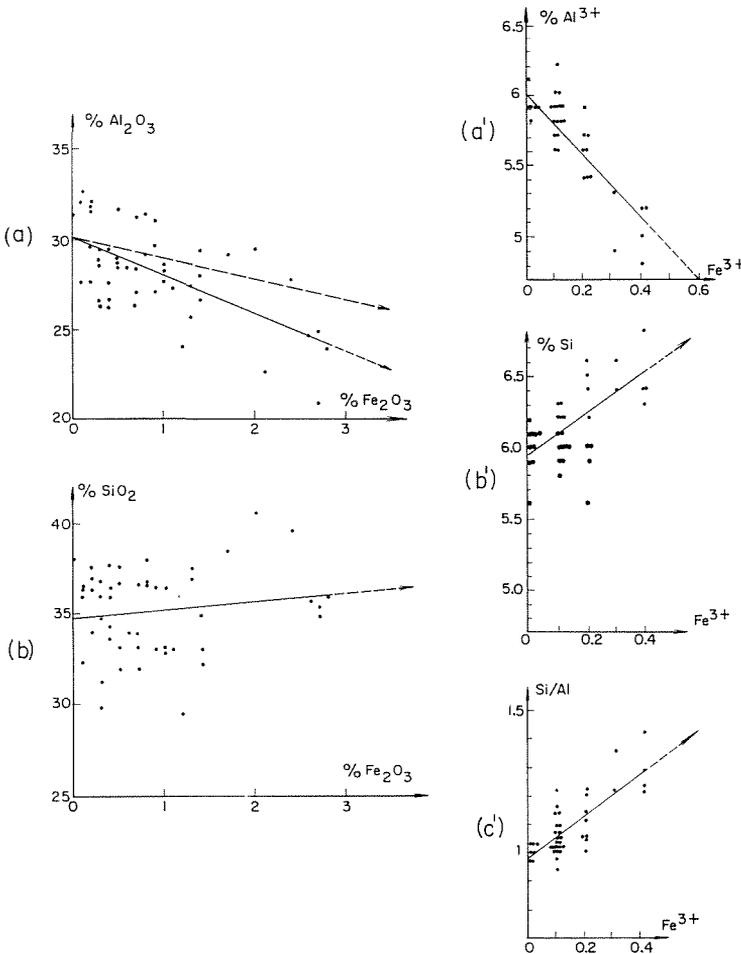
Fig. 3. Lines of correlation of the weight percentage in Fe_2O_3, Al_2O_3 and SiO_2 of the nosean-haüynes. In (a). $(Al_2O_3) = -2.17 (Fe_2O_3) + 30.3$ with $r = 0.717$; whereas the substitution of a Al_2O_3 molecule by a Fe_2O_3 molecule would give a straight line (dotted line): $(Al_2O_3) = -1.275 (Fe_2O_3) + 30.3$. In (a'). $Al^{3+} = -2.35 (Fe^{3+}) + 6.02$; in (b). $(SiO_2) = 0.45 (Fe_2O_3) + 34.82$ with $r = 0.755$; in (b'). $Si^{4+} = 1.41 (Fe^{3+}) + 5.93$; in (c') $\dfrac{Si}{Al} = 0.755 (Fe^{3+}) + 0.98$ with $r = 0.769$.

So (RUCKLIDGE and STUMPFL, 1968) the petzite ($Ag_3Au\ Te_2$) loses Au at the central point and tends towards ($Ag_{3.8}Au_{0.2}\ Te_2$), whereas 5 or $10\,\mu$ further away, the material enriches in Au. When the electron bombardment ceases, the diffusion happens in the opposite direction and the mineral, whose structure has not been destroyed, comes back to its primitive state. Here, the chemical study of the crystal is more difficult to achieve; but it is still possible, provided low powers are used, and this by decreasing either the accelerating voltage, or the beam current (15 kV and $0.05\,\mu$ A or 25 kV and $0.005\,\mu$ A.)

c) In a third sampling, we shall study the glasses, some feldspaths (RIBBE and SMITH, 1966, p. 225), the feldspathoids and the zeolites, considering only the main components of the rocks. What happens here is an *irreversible damage* of the crystal, as marked by the formation of a crater, or of a blister (SCHOLÉS, 1968). The elements Na and K seem to disappear, the contents in Si, Al, Fe increase, these elements can be considered as not, or at least hardly, mobile. The damage is indeed irreversible, for a measure made long after the first analyses shows a percentage in elements identical with that of the last, and not of the first measurements.

We shall show that in these cases the analyses are possible, for the glasses (RIBBE and SMITH, 1966, p. 201) as well as for the feldspathoids, provided they are made under Θ_m temperatures as low as the apparatus permits. Thus, for instance, W_0 must decrease and r_0 increases ($0.01\,\mu$ A and a large spot of $10\,\mu$ for the analysis of glasses) although other factors might come into consideration.

2. Practical Conditions of Measurement

The regulation of the electron current has been maintained within a 1% approximation; yet, since the sample-holder that we used did not allow us to measure the current with the Faraday cylinder, we have used another method of marking the intensities. Thus, day after day, we have maintained constant the number of impulsions emitted by the standard SiO_2 for the $K\alpha$ Si line, by regulating the intensity of the beam. During the experiment, we have also controlled the stabilization of the beam current by checking, every 10 to 15 minutes, that the answers given by the different standards (artificial silica, blue corindon, pure iron) remained constant (1% approximation). Moreover, we have always worked with the same conditions of pre-heating of the apparatus, so as to maintain the gain developped by the whole on a strictly constant basis.

a) Voltage

The systematic attempts at a ratio-analysis of the elements Si, Al and Fe in our feldspathoids (Fig. 4) show that the degradation of these minerals is very fast: the alteration is marked by a constant increase of the contents of the three elements, and a departure of the alkalines. More precisely, the alteration is all the more important as the energy received by the target is greater; so, even at the very beginning and during a short time of irradiation, the damage is important when accelerating voltages superior to 15 kV are used (Fig. 4 A and B). The noted damage is due to a nearly total departure of the alkalines (Fig. 5 A and B); it does not affect the ions of the silicated framework — Si, Al — for the relations between these elements remain constant.

Whatever the gradation of the damage (Fig. 5 C and D), the value of the ratio I_{Al}/I_{Si} remains unchanged. This constancy in the relation of the received intensities shows the maintainance at a fixed value of the relations Al/Si, for even if there is no exact proportionality for one element between the received intensity (I) and its concentration (C), the difference remains slight in the range of the concentrations we studied.

Thus this preliminary study shows that it is necessary to make the measurements during the first 20 seconds of exposition of the target, while it is not yet, or only
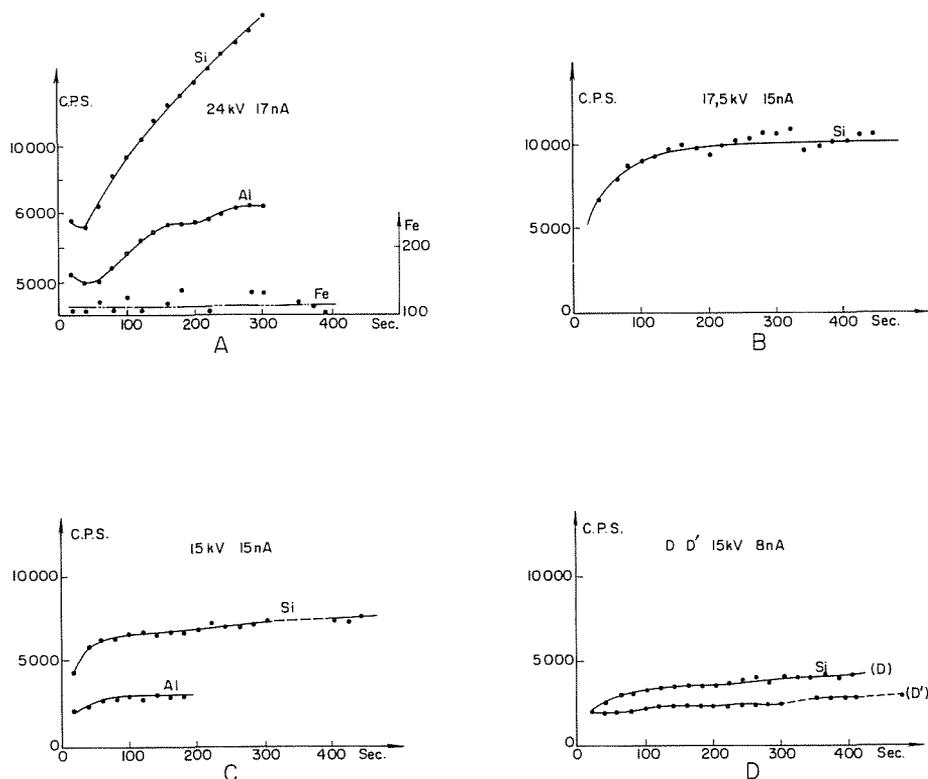
Fig. 4. Variations of the number of impulsions (counts per second, C.P.S.) under different conditions. It will be noted that the impulsions received by the proportional counter and shown on the Y-axis cannot be, from one high voltage to the other, directly compared; for the emission of photons X by the target varies not only with the number of atoms, but also with the accelerating voltage and the electron intensity; the curve D is obtained with a beam diameter of 1 μ, D' with a beam diameter of 10 μ

slightly, modified. Moreover the time of impulsion-counting must be short, of only *20 seconds*, provided (we shall see it later) this lack of statistical information makes a greater number of comparative analyses necessary. Lastly, even for a counting *during the first 20 seconds*, the target must receive a low energy, yet compatible with the possibilities of response from the elements studied. We have kept the conditions of measurement for Si and Al at 17 kV and 8 nA and, for Fe and Ti, values of 22,5 kV and 9 nA. In these conditions, nevertheless, the countings are reproductible even for the Si, Al and Fe. For the latter element the damage of the sample does not give rise to an important variation of concentration as we have shown before (Fig. 4 A).

b) Dimensions of the Analysed Area

Using an defocussed probe, we have analysed an area a larger than usual, of 10 μ of diameter. Fig. 4 D-D, shows that the damage is indeed less important; so, the target shows no change in Si during the first 60 seconds. Theoretically, this method
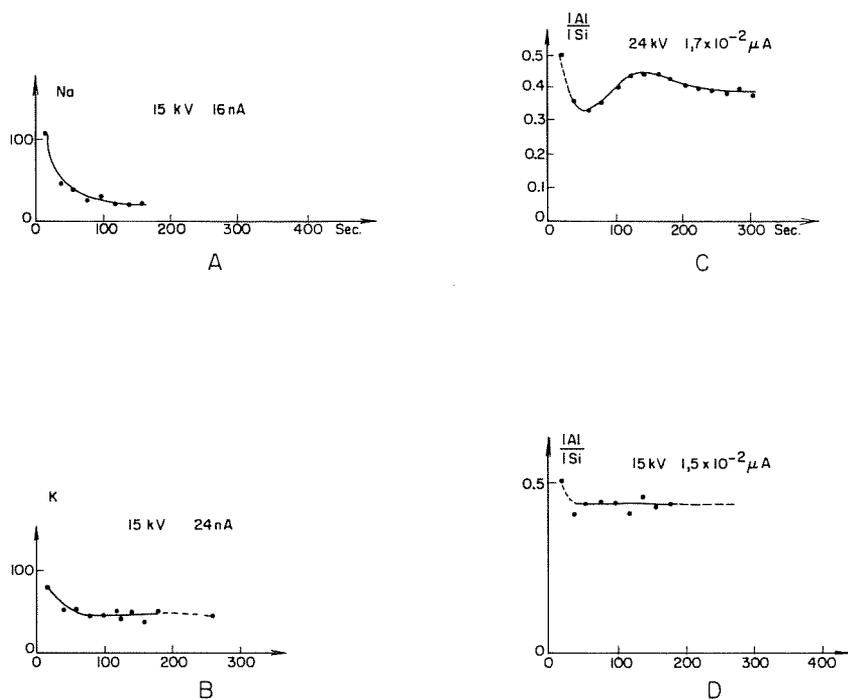
Fig. 5. Variations of the intensities (C.P.S.) or ratios of intensities received under different conditions of electron bombardment plotted versus the bombardment time in seconds

should therefore be the best, but we have not used it because we meant to make all our measurements in the same conditions. And an electron beam diameter of 10μ is much too wide when it comes to analysing the small grains.

We have used the measurements by large surfaces only in the case of heterogeneous zones within the range of square microns, zones in which a measurement with a beam diameter of 10μ allows us to obtain the average concentration in one element.

IV. Analytical Results

Two types of rocks have thus kept our attention; the miaskitic phonolite of the centre of the Massif of Vinsac, and the agpaitic phonolite sampled in the Massif of Auteroche. We shall give the results obtained in both cases, then we shall compare them, and lastly will be able to integrate them into the study of the petrogenesis of alkali rocks.

1. Analysis of the Noseans of the Miaskitic Phonolite

In this case, the nosean appears at two generations. The phenocrystals, from 300μ to 1 mm, have a light rim, whereas their middle part is dark; the central part can be again of a light colour (as in phenocrystal A, Fig. 6), or can be a dark extension of the middle area (as in phenocrystal B, Fig. 6). The areas presented here are of a

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Si/Al	$\frac{Al+Fe}{Si}$
32.5	21.9	1.21	1.26	0.820
		0.96		
32.8	22.3	3.4	1.25	0.883
33.0	22.5	0.77	1.24	0.814
33.4	22.1	0.87	1.26	0.797
33.6	22.5	0.61	1.28	0.806

⌐——————⌐ 100 μ
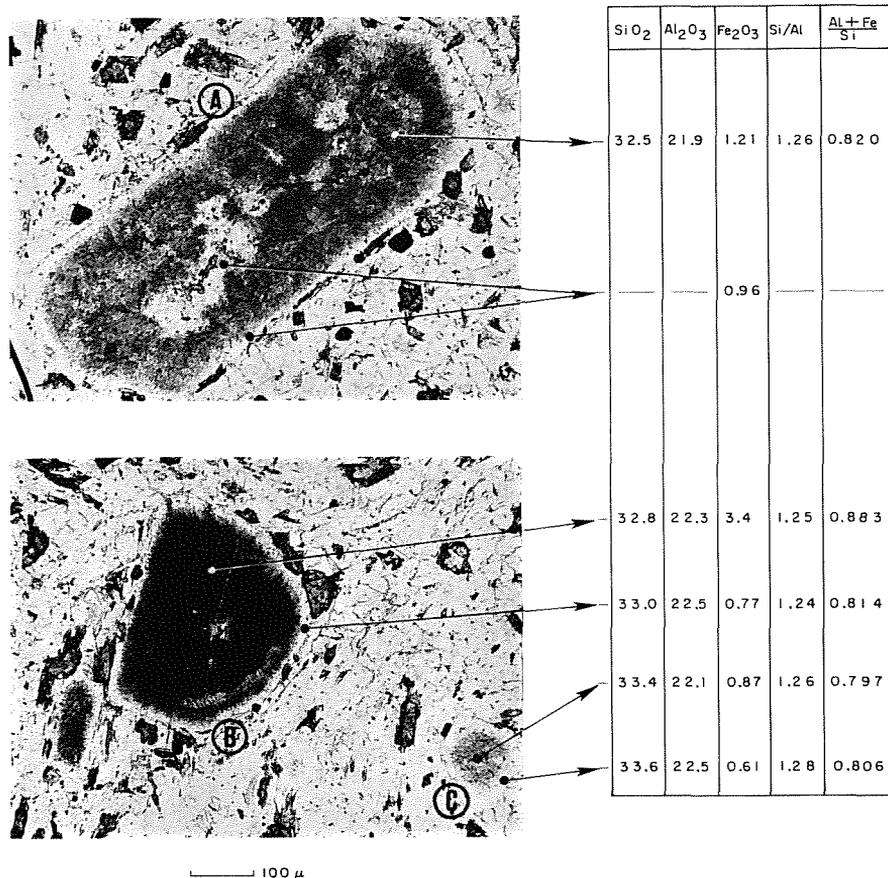
Fig. 6. Micrographs of the miaskitic phonolite of the centre of the massif of Vinsac, with the results of the chemical compositions of the corresponding noseans. The results for SiO$_2$ are given at $\pm$ 0.4%, those of Al$_2$O$_3$ at $\pm$ 0.5%, and, lastly, of Fe$_2$O$_3$ from $\pm$ 0.17% to $\pm$ 0.4% depending on the contents from 0.61 to 3.4

simple type, but it often occurs that alternating light and dark stripes should be more numerous (Fig. 1).

As for the microcrystals, of about 150μ, they show two areas at the most: the inside is dotted with black and the outside area is clear (C, Fig. 6). In many cases, the whole microcrystal is quite clear and shows no inside punctuation.

In all cases (Fig. 6), the black coloration corresponds to an enrichment in iron; especially, the white areas, either inside or outside, are poorer than the middle blackened area, while they keep the same iron content. So our samplings prove a fixation of iron in certain areas, and not a gradient of progressive iron concentration.

Yet the clear areas do contain a not negligible percentage in Fe, approaching 0.6 to 1%.

As for the darkening intensity, it goes together with the increasing contents in iron, ranging from 0.9% — maximum iron content in the clear areas — to 3.4%.

Moreover, the ratios Si/Al and $\frac{Al + Fe}{Si}$ both increase when the iron content of the feldspathoids increases.

Lastly we must note the following observation concerning the silica contents of the phenocrystals and of the microlites: these crystals of the ultimate generation are the richest in silica, while the poorest in iron.

The iron traced in the analysed feldspathoids can be either found as an ion substituted in the network, as we had earlier suggested, or as micrograins of iron oxide (0.1μ) in the lacking areas (preferably along 100). It seems that the latter solution must be kept as far as the miaskitic phonolites are concerned: for the spreading of the whole counts (150 to 250%) is much greater than the statistical count accuracy, which is here, in each measurement, of about 50%. Yet we cannot make sure whether this actual heterogeneity is secondary, as the result of an exsolution, or primitive.

2. Analysis of the Sodalites of the Agpaitic Phonolite

There are three kinds of crystals: all characterized by the fact that their black areas have a homogeneous coloration, so intense that the mineral can appear as an opaque body (Fig. 7):

the first generation, megacrystals ranging from 500 to 200 μ, is exceptional; it is represented by sodalites with a white but heterogeneous core, all the more developped as the crystal is larger (D and E, Fig. 7); the core is followed by a black rim, then sometimes by a colourless fringe;

the phenocrystals of the second generation (about 100μ) represent a relatively important part of the feldspathoids. They are uniformly blackened (F, Fig. 7).

Lastly the microcrystals (G, Fig. 7), ranging from 30 to 40μ, are similar to the miaskitic phonolites in so far as they also show two areas, a dark centre and a light outside. Naturally, the depth of coloration is not the same for the microcrystals of two different kinds of phonolites.

Thus we find similar results to those above, in so far as iron marks the dark areas. Yet here the gradient of concentration of the dark areas, and the outside ones is richer in Fe than the central (F) or pericentral (E) areas. This gradient does not correspond with a difference in coloration optically perceivable.

Similarly, the white colourless areas do not entirely lack Fe; yet in this case there is a disparity between the core (0.2%) and the outside (over 1%).

Once again, the content in silica increases from the crystals of the first generation to those of the groundmass.

Yet an important difference must be noted between the feldspathoids of the two kinds of phonolites as far as the location of the iron is concerned. In the agpaitic phonolites, the iron seems to be a sodalite-structured iron, for the dispersion of the counts is low; the practical (ranging from 40 to 50%) and theoretical (30%) dispersions being of a similar rate.

Fig. 7. Micrographs of the agpaitic phonolite of Auteroche, with the results of the chemical compositions of their sodalites. The results are given with the same approximations as in Fig. 6. D and E: Megacrystals with white centre, black rim and sometimes (D) white external zone. (*Erratum in D* = the arrow from the black area should indicate a percentage of 1.97 Fe_2O_3, which has been omitted in the third column.) F: Phenocrystal wholly black. G: Microcrystals with black centre and white rim

	SiO_2	Al_2O_3	Fe_2O_3	Si/Al	$\dfrac{Al+Fe}{Si}$
	3 4.1	—	0.21	—	—
	3 6.3	2 2.7	1.07	1.36	0.7 5 7
	—	—	0.53	—	—
	—	—	1.1 ↓ 2.7	—	—
	3 5.9	2 3.2	1.85 ↓ 3.00	1.31	0.8 1 4
Mean	3 6.6	2 3.1	2.30	1.35	0.7 9 0
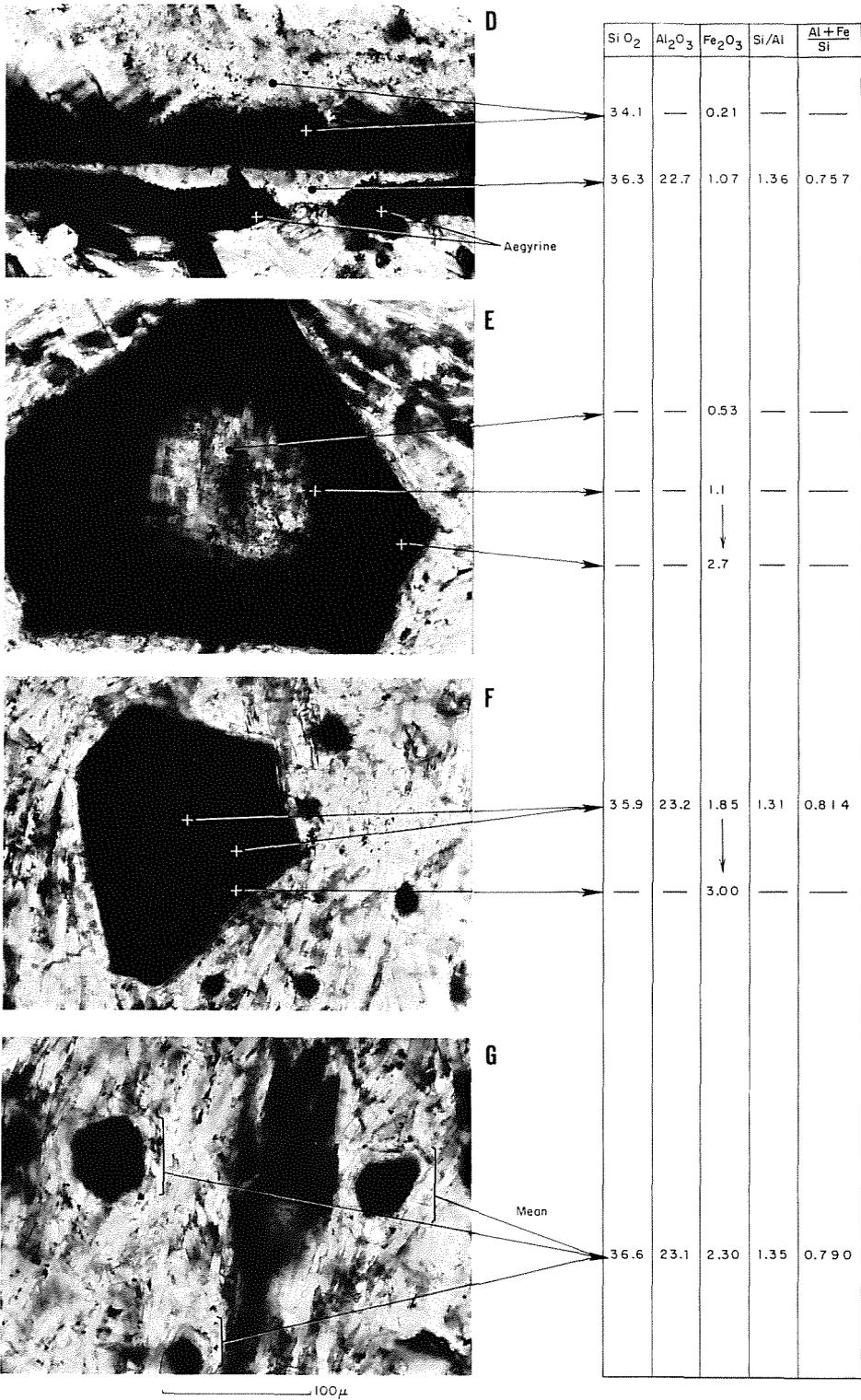
Fig. 7
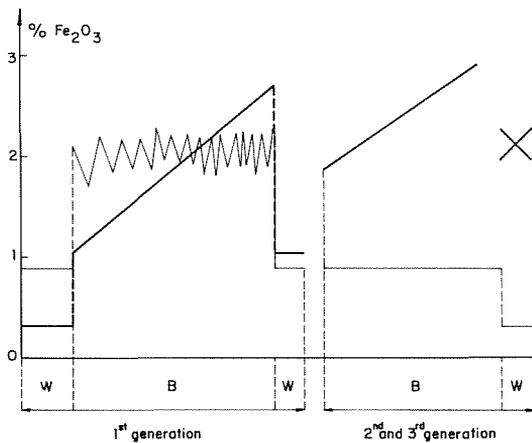
Fig. 8. Diagram of the evolution of the feldspathoids with white areas (*W*) and with black areas (*B*) in the agpaitic phonolites (thick line) and the miaskitic phonolites (thin line). For each generation of crystals the diagram is given from the core (left) to the margin (right). For the agpaïtic phonolite, the evolution is obtained from the data of Fig. 7 with 1st generation: Megacrystals D.E; 2nd generation: Phenocrystal F; 3rd generation: Microcrystals G. For the miaskitic phonolite, the evolution is obtained from the data of Fig. 6 with 1st generation: Phenocrystal A and 2nd generation: Microcrystals B.C.

3. Comparative Importance of Fe in Both Types of Phonolites

A comparison of the various generations of feldspathoids of the two types of phonolite, neglecting size-differences (the crystals are larger in the miaskitic phonolites) is showed in Fig. 8.

We can then notice a succession of nearly identical white and black areas, the dark colour appearing only when the Fe_2O_3 content is superior to 1%.

An essential difference, though, concerns the behaviour of the iron, whose weight percentage increases from one generation to the other in the feldspathoids of the agpaitic phonolites, whereas it decreases in those of the miaskitic phonolites.

One could at first glance interpret this as a greater Fe content in the agpaitic phonolites, and even more in their last phases of crystallization. Yet the global chemical analyses provide a better explanation: the agpaitic magma is mainly made of Fe^{+++}, whereas the miaskitic magma contains mainly Fe^{++}.

Thus agpaitic minerals contain Fe^{+++}: e.g. aegyrine, Fe^{+++}-sodalite, and probably Fe^{+++}-feldspaths (BAILEY and TILLEY, 1966), whereas miaskitic phonolites contain Fe^{++} minerals: augite, magnetite, nosean with iron oxide inclusions. To this must be added a difference related with the progressive or discontinuous mode of fixation of the iron. In the miaskitics, the iron is mixed into the magnetites, the augites, so that its residual importance becomes subsidiary. Inversely, no early mineral of the agpaits fixes Fe, and the latter concentrates in the residual areas in which only aegyrine and feldspathoids appear.

The present study seems to prove that the iron is indeed substituted into the structure of the feldspathoids, instead of Al; moreover it is proved that the sub-

stitution is conditionned by the partial oxygen pressure of the surroundings, which must contribute to the richness in Fe^{+++}.

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