

Mineralogy and Geochemistry of the Neogene Andesites from Annaba's Area (Northeast Algeria)-Calcic Amphibole Thermobarometry

Daif Menana and Arafa Ahmed

Département de Géologie, Université de Annaba B.P.12; 23000, Algeria

Abstract: Neogene Andesites are part of an igneous series that outcrops in the Northeast of Algeria and that belongs to Maghreb's magmatic margin belt. This series is composed of calc-alkaline rocks including essentially microgranites, rhyolites and diorites and well expressed andesites. Andesites consist of complete differentiated succession including scarce basalts, small amounts of rhyolites and preponderant andesites and dacites. They are heterogeneous in texture, colour and structure but intimately related to each other in time, space, mineralogical and chemical features. They also have a particular mineralogy: olivine is lacking, orthopyroxene is restricted to basic andesites which are less common whereas plagioclases, clinopyroxenes and hydrous minerals are abundant, titanomagnetite, ilmenite and sphene are also present in small quantities. The salient geochemical characteristics of these rocks are high SiO_2 , K_2O , Rb and low FeO^T , MgO , CaO , Ba and Sr. They also show an enrichment in light Rare Earth Elements (REE) and a depletion in heavy REE. Whole rock $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios are high and unequal (from 0.707-0.710). All these features testify that investigated andesites are mostly acid, medium to strongly potassic and are typical of calcalkaline suites of continental margins. The amphiboles represent an important ferromagnesian phase, it seems advantageous to examine more closely their composition. Detailed microprobe analysis shows that all amphiboles are calcic, silica poor, magnesian, weakly titaniferous and most of their aluminium is in tetrahedral site. They may be divided into two sub-groups: On the one hand the magnesiohastingsite, pargasite and kersutite group, on the other the tschermakite group (according to classification of Leake, 1997). Chemical composition of amphiboles allows thermobarometric investigations. The Aluminium in Hornblende (AH) barometer is used to estimate pressures (P_1 , P_2) with two different calibrations (Hollister *et al.*, 1987 and Schmidt, 1992). Temperatures (T_1 , T_2) are calculated using Ti in amphiboles thermometry (Otten, 1984 and Féménias *et al.*, 2006) compared to plagioclase + hornblende thermometer of Blundy and Holland (1990). In all studied rocks, amphiboles phenocrysts equilibrate at nearly constant pressure of 5 ± 0.5 Kbar. But their temperatures of crystallization range from 800-950°C (T_1 from 850-950°C, T_2 from 800-900°C) with a slight decrease in dacites and rhyolites. These conditions correspond to a shallow crustal chamber and may explain most of andesite features: Zoning in phenocrysts, high SiO_2 , K_2O and abundance of pyroclastic forms.

Keywords: Algeria, neogene, calc-alkaline, potassic andesites, Ca-amphiboles, thermobarometry

INTRODUCTION

Andesites studied are a part of igneous series that extend for about 70 km² between Chetaibi and Cap de Fer in the eastern Algerian coast. They are settling within Cretaceous and Oligocene flyschs and are contemporaneous of Miocene formations. Their K/Ar radiometric datings give an age of 15.1-15.9 Ma according to Bellon (1976) and Marignac (1983).

The igneous series includes volcanic, subvolcanic and plutonic rocks (Fig. 1). On the basis of their nature and field relationship these rocks have been judiciously divided into four main groups: Microgranites, rhyolites, diorites and Andesites groups (Hilly, 1957).

Thus, in addition to the andesitic group, which is the main matter of this paper, it is established that the

widespread group is the microgranitic one comprising massive and brecciated forms. In fact, it is composed of a great part of micromonzogranites, some microgranodiorites and rare true microgranites whereas less acid specimens are met in dioritic and tonalitic enclaves. Its paragenesis is constant with phenocrysts of plagioclases, embayed quartz, biotite, K-feldspar in a fine grained matrix of interstitial quartz and feldspar.

If we exclude the rhyolites from Eastern outcrops which are deeply altered and particularly alkaline, the rhyolitic group has slightly the same features found in microgranites. Dioritic group with several sills and small laccolites mainly includes diorites, some microdiorites, tonalities and a limited quantity of gabbros or microgabbros. Its paragenesis is similar to that of andesitic group: Plagioclase, pyroxene, amphibole and biotite.

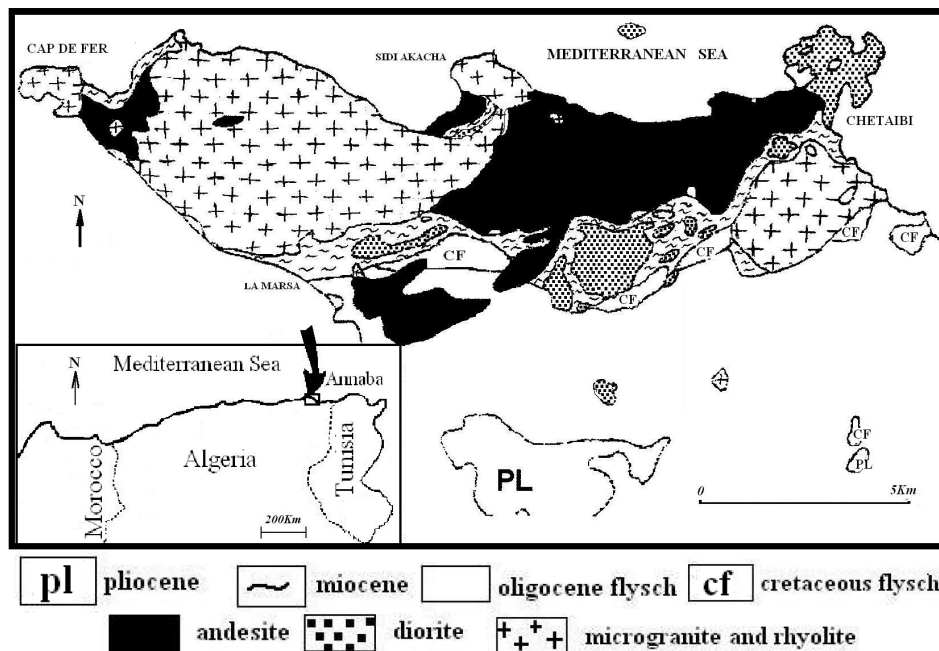


Fig. 1: Simplified geologic map of the N.W. Annaba area (after Hilly, 1962; modified) and inset location map

The genesis of this series, previously considered as complex because difficult to explain according to usual subduction process, has been resolved late years by a slab breakoff model as proposed by Maury *et al.* (2000). Most recent authors are in agreement with this model and therefore, making it easier to explain the origin of these rocks.

The main purpose of this paper is to point out particular features of Andesites. Using microprobe analysis; the paper attempts to establish an accurate chemical composition of different minerals and particularly the amphiboles. These data thus make it possible to compute pressure and temperature estimates of crystallization based on Al and Ti contents thermobarometry.

MATERIALS AND METHODS

Twenty samples are considered for major and trace elements analysis, four samples for Sr isotopes and five for Rare Earth Elements. For microprobe study eight thin sections are selected from 3 Andesites (A), 3 Dacites (D) and 2 Rhyolites (R). All samples are from Chetaibi- Cap de Fer region. Major and trace elements are analyzed using X ray fluorescence at the University of Nancy I (France).

Rare Earth Elements and $^{87}\text{Sr}/^{89}\text{Sr}$ are carried out using isotopic dilution on mass spectrometry at CAESS University of Rennes (France). Major element compositions of all mineral, particularly of amphiboles and plagioclases are determined by electron microprobe

(CAMEBAX) at the Centre of "Microsonde Ouest", IFREMER-Brest (France) using a combination of natural and synthetic mineral standards. Operating conditions are: Accelerating voltage of 15Kv, current of 10nA-20nA and counting time from 6s for Cr to 24s for Na.

Structural formulas for amphiboles are calculated following the method of Cosca *et al.* (1991), Fe^{2+} and Fe^{3+} are estimated using normalization schema based on $\text{Si}+\text{Ti}+\text{Al}+\text{Fe}+\text{Mg}+\text{Mn}=13$ cations per 23 oxygens. Structural formulas of plagioclases are calculated on an anhydrous basis of 8 oxygens. Altered phenocrysts presenting gulfs or patches are omitted.

Samples chosen for barometric and thermometric investigation have the full required assemblage with hornblende in textural equilibrium with plagioclase, biotite, K-feldspar, small amounts of quartz, sphene and Fe-Ti oxides. They also satisfy oxygen fugacity condition f_{O_2} with $\text{Mg} / \text{Mg} + \text{Fe}^{2+}$ ratios (0.63-0.83) and $(\text{Fe}^{3+} / \text{Fe}^{\text{T}}) > 0.2$ (Anderson and Smith, 1995).

In the samples available, plagioclase is often zoned; the general order of crystallization shows that amphiboles appear to have been formed after plagioclase, consequently amphiboles may be considered as contemporaneous with coexisting plagioclase rims. Therefore, microprobe measures are carried out on plagioclase rims.

When using plagioclase + hornblende thermometer of Blundy and Holland (1990) mole fraction of albite in analyzed plagioclase varies between 0.40 and 0.63.

Table 1: Chemical analyses of three typical andesites (trace and major elements)

					1	2	3
				SiO ₂	59.84	65.28	68.77
				Al ₂ O ₃	15.84	15.15	13.85
				MnO	0.09	0.06	0.04
				MgO	2.93	1.39	0.26
				CaO	5.1	4.14	2.56
				Na ₂ O	3.69	3.34	3.61
				K ₂ O	2.71	4.13	3.99
				TiO ₂	0.72	0.51	0.81
				P ₂ O ₅	0.15	0.05	0.27
				LOI	2.89	1.54	1.6
				Sum	99.63	98.81	98.72
Sr	206	173	163				
Rb	145	256	169				
Co	15	10	10				
V	143	113	101				
Ni	26	10	79				
Cr	41	41	13				
Ba	263	355	307				
Rb/Sr	0.7	1.48	1.04				

RESULTS AND DISCUSSION

Andesite characteristics

Petrography: Andesitic-group covers around 25 Km² and presents a wide range of colours and structures. Four facies are distinguished: Andesites (stricto-sensu), dacites, discrete amounts of rhyolites and strongly rare basalts (Fig. 2). Pyroclastic Andesites are widespread and characterized by their poor sorting producing various breccias. Massive Andesites are essentially composed of flow, dikes (with chilled margins) and pillow-lavas.

In spite of this huge heterogeneity andesites contain a constant paragenesis including plagioclase, pyroxene, amphibole, biotite and a small quantity of quartz and K-feldspar. They are highly porphyritic and contain up to 60 vol % phenocrysts sized 0.5-5.mm. They exhibit a large variety of texture: Glassy, microlitic, vesicular... However the glomeroporphyritic texture is the most distinctive. The groundmass is often intersertal, more or less glassy and includes minute plagioclases, ferromagnesian granules and quartz-feldspar intergrowth. In the andesitic group: Olivine is lacking, orthopyroxene is confined to basic andesites which are rather limited, whereas amphiboles may represent an important mineral phase recording crystallization history.

Geochemistry: Chemical composition of andesites indicates high SiO₂, K₂O and low FeO^T, MgO, CaO (Table 1). Major element compositions show that these rocks consist dominantly of acids andesites followed by dacites, small amounts of rhyolites and strongly rare basalts.

Trace elements are significantly enriched in Rb, Cs, U, Th whereas Sr and Ba are depleted. Compatible elements (Cr, Ni, Co, V, Sc) are moderate. These rocks also show enrichment in high Rare Earth Elements (REE) and depletion in heavy REE, (Fig. 3).

Whole rock ⁸⁷Sr / ⁸⁶Sr ratios of four samples vary from 0.707-0.710 testifying a complex genesis (Arafa, 1990a). The chemical composition of the basaltic specimen is similar to those of high alumina Basalts.

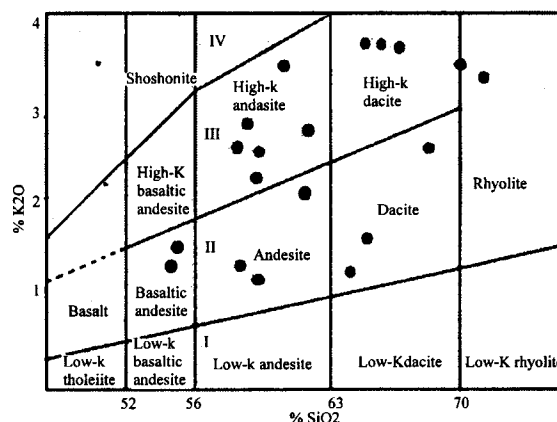


Fig. 2: Classification of the studied andesites (?) in the discriminant diagram of Peccerillo and Taylor (1976). I = tholeiite series, II = calc-alkaline series, III = high-K calc-alkaline series, IV = shoshonite series

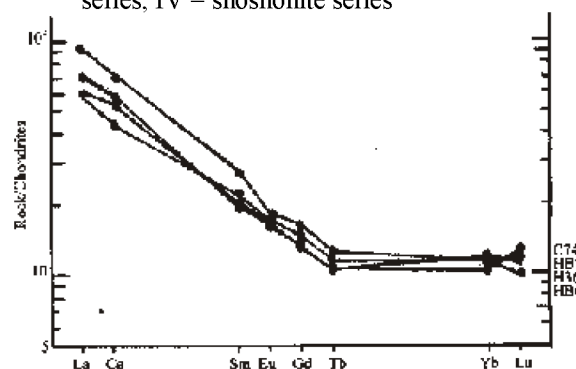


Fig 3: Patterns of rare earth elements from studied andesites

Petrographical and geochemical study corroborate their belonging to a calc-alkaline series of active continental margin (Arafa, 1986, 1990b), (Fig. 4.).

Mineralogy: Plagioclases are ubiquitous and the most abundant minerals. Often twinned and strongly zoned they cover a large range of composition from bytownite An₈₈ to an andesine An₃₅ (Table 2).

Tabale 2: Representative microprobe analyses of plagioclases from various andesites, structural formulas calculated on the basis of 8 oxygens. (FeO^T = total iron as FeO)

	1	2	3	4	5	6
FeO ^T	0.31	0.68	0.88	0.40	0.09	0.08
Na ₂ O	1.48	2.94	4.31	5.45	6.33	7.20
SiO ₂	46.25	51.19	53.42	54.86	57.88	59.94
K ₂ O	0.00	0.16	0.29	0.39	0.42	0.59
MnO	0.00	0.01	0.00	0.03	0.09	0.00
MgO	0.08	0.09	0.14	0.03	0.00	0.00
Al ₂ O ₃	33.60	32.26	29.21	28.71	26.39	25.51
CaO	17.48	14.19	12.61	10.84	8.53	7.21
Cr ₂ O ₃	0.00	0.00	0.06	0.00	0.12	0.00
TiO ₂	0.00	0.00	0.08	0.00	0.06	0.00
SUM	99.20	101.52	101.00	100.71	99.91	100.53
Fe	0.01	0.03	0.03	0.02	0.00	0.00
Na	0.13	0.26	0.38	0.47	0.55	0.62
Si	2.15	2.30	2.41	2.47	2.60	2.66
K	0.00	0.01	0.02	0.02	0.02	0.03
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.01	0.01	0.01	0.00	0.00	0.00
Al	1.84	1.71	1.55	1.52	1.40	1.34
Ca	0.87	0.68	0.61	0.52	0.41	0.34
Cr	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00
SUM	5.00	4.98	5.01	5.02	4.99	5.00
AB	0.13	0.27	0.38	0.47	0.56	0.62
OR	0.00	0.01	0.02	0.02	0.02	0.03
AN	0.87	0.72	0.61	0.51	0.42	0.34

In groundmass they are more sodic and usually have similar contents as those of phenocrysts rims. Andesites are almost without olivine which appears as “ghost”. It is always pseudomorphosed and altered to fibrous particles or with disengagement of iron oxide grains.

Orthopyroxenes, present in small amounts are often altered and confined to basic andesites. Their analyses are not conclusive and only indicate a slight Mg character. Clinopyroxenes, represent around 5 vol % as phenocrysts. Their compositions are almost constant with W₃₅₋₄₅, En₃₅₋₅₀ and Fs₇₋₂₅. They correspond to augites with rare endiopsides (Deer *et al.*, 1965). Biotite phenocrysts are frequent in intermediate and acid andesites. They coexist less frequently with pyroxenes than with amphiboles. Though sometimes chloritized, several biotite phenocrysts are primary and stable. Most of studied biotites are magnesian and slightly feriferous in groundmass and rhyolites.

Andesites contain 2-5 vol % amphiboles as phenocrysts. The hornblende is the only one amphibole that occurs; green or brownish it is widespread in intermediate and acid andesites where it can reach until 25 vol % of crystals. In thin sections hornblende often shows well developed prismatic phenocrystals (size 0.5-3mm). It coexists with plagioclase, augite and more frequently with biotite. It seems to be less frequent in groundmass. In some samples, hornblende appears at the expense of pyroxenes and shows their relicts. However, a large amount of amphiboles are well developed and without any resorption especially in glassy matrix. They undoubtedly indicate an igneous primary origin.

K-feldspar in small amounts is generally associated with quartz microcrysts in interstitial spaces particularly

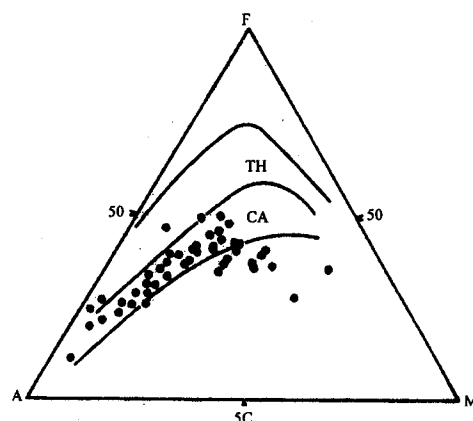


Fig. 4: AFM diagram of the studied igneous rocks A=Na₂O+K₂O, F=FeO+0.9Fe₂O₃, M=MgO. TH=tholeiitic suite, CA=calcalkaline suite (Kuno, 1968)

in differentiated terms. Two oxides occur in andesites, titanomagnetite and ilmenite as inclusions in phenocrysts or as groundmass grains. Apatite, zircon and sphene are also present. Late magmatic silicification is represented by chalcedony or opal that may fill up pores and joints. The abundance of plagioclase and hydrous minerals, chemical nature of pyroxene, amphibole and biotite are typical of a calcalkaline series (Gill, 1981).

Amphibole chemical compositions: As amphiboles represent an important phase, involved in magmatic differentiation and recording conditions of crystallization (Allen and Boettcher, 1978), it appears fruitful to study their composition, (Table 3).

Studied amphiboles are silica poor; Si contents average 6.35 apfu (atoms per formula unit). They show limited variations and are independent from their SiO₂ host rocks. CaO has a limited range of content (from 11.03 to 11.6 %) and Ca is always above 1.7 apfu. Na₂O contents lie between 1.6 and 2.2 %. Na^A is always > to Na^{M4}.

In agreement with the potassic feature of the whole rock, K₂O contents are high (from 0.8 to 1.2 %)

Al₂O₃ is around 10 % and all samples exhibit low Al^{VI} and high Al^{IV} contents which makes more than 90% of Al in the tetrahedral site. TiO₂ contents average 2.5%. They show lower contents in dacites and rhyolites and can reach 3.2% in some andesites. Ti contents are higher than 0.25 apfu making amphiboles weakly titaniferous. FeO^T contents are moderate (from 12 to 16 %). Most of the amphiboles are characterized by a low Fe³⁺ and a high Fe²⁺ contents (0.53-0.9 and 0.62-1.20 apfu respectively) and Fe³⁺/Fe²⁺ ratios correlate positively with the brownish colour of amphiboles. X_{Mg} = (Mg /Mg + Fe²⁺) ratio varies between 0.69 and 0.83 and increases slightly from andesites to rhyolites.

Table 3: Microprobe analyses of amphibole from studied andesites and thermobarometry: Pressures P_1 - P_2 ; temperatures T_1 - T_2 successively based on calibration of Hollister *et al.*, 1987; Schmidt, 1992; Féménias *et al.*, 2006 and Blundy and Holland, 1990, (A: Andesite, D: Dacite, R: Rhyolite; c: core, r: rim)

Sample	A	A	A	A	A	A	A	A	A	D	D	D	D	D	D	D	D	R	R	R
	r	c	r	c	r	c	r	c	R	r	c	r	c	r	c	r	c	r	c	c
FeO ¹	14.04	13.58	15.06	13.95	12.93	13.81	15.51	15.19	13.87	14.42	14.38	12.67	13.55	13.41	13.78	15.98	11.99	15.64	14.87	12.62
Na ₂ O	1.98	2.19	1.88	2.06	2.13	2.12	1.81	2.08	2.11	2.04	2.03	1.77	2.09	1.94	1.91	2.08	2.17	1.84	1.97	2.00
SiO ₂	43.06	43.34	43.63	44.39	43.68	43.62	43.90	43.89	43.44	43.67	43.39	43.96	43.46	43.76	44.36	44.37	43.62	43.51	43.42	42.93
K ₂ O	0.89	1.00	0.99	0.88	1.01	0.81	0.94	0.98	0.92	0.86	0.93	0.89	0.96	1.09	0.97	1.04	1.00	0.91	1.07	0.90
MnO	0.00	0.14	0.16	0.17	0.16	0.24	0.41	0.26	0.37	0.34	0.31	0.30	0.31	0.27	0.00	0.06	0.08	0.37	0.27	0.08
MgO	12.99	13.41	12.48	13.85	14.04	13.51	12.94	12.67	13.07	12.86	12.59	14.29	13.72	13.19	13.45	12.55	14.02	12.28	12.42	14.28
Al ₂ O ₃	10.70	10.12	10.49	9.53	10.18	10.02	9.76	10.24	10.01	10.59	10.27	10.63	9.75	10.00	9.49	9.87	10.72	9.91	9.77	11.24
CaO	11.15	11.47	11.33	11.42	11.30	11.19	11.48	11.39	11.03	11.12	11.35	11.31	11.06	11.18	11.17	11.14	11.29	11.14	11.20	11.27
Cr ₂ O ₃	0.03	0.06	0.14	0.05	0.00	0.00	0.00	0.16	0.05	0.00	0.00	0.00	0.07	0.06	0.00	0.01	0.01	0.11	0.04	0.00
TiO ₂	3.06	3.26	3.13	2.91	2.90	3.02	2.94	2.96	2.97	2.39	2.79	2.40	2.63	2.77	2.60	2.81	2.87	2.36	2.78	2.60
Sum	97.89	98.56	99.28	99.21	98.33	98.35	99.67	99.81	97.85	98.28	98.04	98.22	97.58	97.67	97.73	99.91	97.76	98.06	97.80	97.91
Fe ³⁺	0.71	0.53	0.65	0.71	0.68	0.74	0.83	0.66	0.68	0.78	0.57	0.90	0.81	0.58	0.64	0.72	0.53	0.82	0.59	0.91
Fe ²⁺	1.01	1.12	1.17	0.97	0.89	0.93	1.04	1.18	1.01	0.98	1.20	0.62	0.84	1.07	1.05	1.21	0.92	1.10	1.25	0.61
NaM ⁴	0.26	0.21	0.24	0.24	0.25	0.26	0.21	0.24	0.27	0.27	0.22	0.26	0.27	0.25	0.25	0.28	0.24	0.25	0.23	0.26
Na ^A	0.30	0.41	0.29	0.34	0.35	0.34	0.30	0.34	0.33	0.31	0.36	0.24	0.32	0.31	0.29	0.30	0.37	0.27	0.33	0.30
Si	6.28	6.31	6.32	6.39	6.33	6.33	6.33	6.33	6.35	6.34	6.36	6.32	6.35	6.41	6.47	6.39	6.34	6.37	6.40	6.20
K	0.17	0.19	0.18	0.17	0.19	0.15	0.17	0.18	0.17	0.16	0.17	0.16	0.18	0.20	0.18	0.19	0.19	0.17	0.20	0.17
Mn	0.00	0.02	0.02	0.02	0.02	0.03	0.05	0.03	0.05	0.04	0.04	0.04	0.04	0.03	0.00	0.01	0.01	0.05	0.03	0.01
Mg	2.83	2.91	2.69	2.97	3.03	2.92	2.76	2.72	2.85	2.79	2.75	3.06	2.99	2.88	2.93	2.69	3.04	2.68	2.73	3.07
Al ^{IV}	1.72	1.69	1.68	1.61	1.67	1.67	1.66	1.67	1.65	1.66	1.64	1.68	1.65	1.59	1.53	1.61	1.66	1.63	1.60	1.80
Al ^{VI}	0.12	0.05	0.11	0.01	0.07	0.04	0.00	0.07	0.08	0.16	0.14	0.12	0.03	0.14	0.11	0.07	0.18	0.09	0.09	0.11
Ca	1.74	1.79	1.76	1.76	1.74	1.74	1.77	1.76	1.73	1.73	1.78	1.74	1.73	1.76	1.75	1.72	1.76	1.75	1.77	1.74
Cr	0.00	0.01	0.02	0.01	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00
Ti	0.34	0.36	0.34	0.32	0.32	0.33	0.32	0.32	0.33	0.26	0.31	0.26	0.29	0.31	0.29	0.31	0.31	0.26	0.31	0.28
X _{Mg}	0.74	0.72	0.70	0.75	0.77	0.76	0.73	0.70	0.74	0.74	0.70	0.83	0.78	0.73	0.74	0.69	0.77	0.71	0.69	0.83
(Na+K) ^A	0.47	0.59	0.47	0.50	0.54	0.49	0.47	0.52	0.50	0.47	0.54	0.40	0.50	0.51	0.47	0.49	0.56	0.44	0.53	0.47
P1	5.62	5.04	5.34	4.37	5.05	4.91	4.59	5.06	4.97	5.48	5.25	5.40	4.70	4.98	4.45	4.70	5.60	4.89	4.81	6.03
P2	5.75	5.26	5.51	4.69	5.27	5.15	4.88	5.28	5.20	5.63	5.44	5.57	4.98	5.21	4.76	4.97	5.73	5.13	5.07	6.10
T1	932	953	938	913	913	927	915	918	924	855	903	853	885	909	882	901	911	854	904	878
T2	906	909	903	902	901	901	907	891	886	892	849	845	843	885	872	891	896	805	843	839

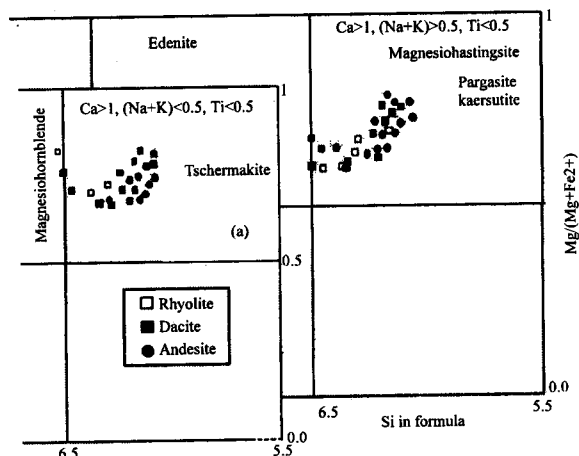


Fig. 5a,b: Amphibole composition (Atoms per formula unit) from studied andesites. Nomenclature after Leake *et al.* (1997)

Nomenclature of amphiboles: According to the IMA classification proposed by Leake *et al.* (1997, all the amphiboles are calcic ($\text{Ca}^B \geq 1.50$ apfu) (Fig. 5a, b) and belong to two sub-groups (Fig. 2):

Group (a) is defined by $(\text{Na} + \text{K})^A \leq 0.5$ apfu (from 0.4-0.5) and mostly contains low Si ($\text{Si}^T < 6.5$ apfu) which is typical of tschermakite. Group (b): defined by $(\text{Na} + \text{K})^A > 0.5$ apfu and contains low Si ($\text{Si}^T < 6.5$ apfu) which is characteristic of magnesiohastingsite, pargasite and kaersutite.

In spite of their limited range of composition it seems that amphibole cores correspond to

magnesiohastingsite, pargasite and kaersutite whereas rims are mostly tschermakitic. Regardless of the amount of $(\text{Na} + \text{K})^A$, all the X_{Mg} range within 0.5 and 1.0 making all the amphiboles magnesian. All analyses are closely conform to the relationship predicted by the tschermak substitution.

Thermobarometry

A. H. barometry: To estimate crystallization pressure in andesites the aluminium in hornblende barometer (A H barometer) is used. A H barometer calibration ($P_1 = 5.64 \text{ Al}_T - 4.76$) proposed by Hollister *et al.* (1987) is chosen and results (P_1) are compared to those obtained by using a second experimental calibration published by Schmidt (1992): $P_2 = 4.76 \text{ Al}_T - 3.01$.

In these formulations P is pressure in Kbar and Al_T is the total Al contents of hornblende. In all rocks amphiboles are equilibrated at about the same pressure: $P_1 = 5.01 \pm 0.37$ Kbar; $P_2 = 5.24 \pm 0.31$ Kbar.

Determined pressures are similar with an average of $5 \text{ Kbar} \pm 0.5$ (Table 3). However a pressure estimate for the last rhyolite (R c) is abnormally high (6Kbar) and may be justified by the fact that its whole rock (up to 73 % SiO_2) is out of silica range of calibration.

Thermometry: Amphiboles from Northwest Annaba andesites average 2.5 % TiO_2 , coexist with Ti rich minerals (ilmenite, sphene), thus they may be considered as Ti saturated. Considering the reduced pressure domain (≈ 5 kbar), the whole rock nature (extrusive and calc-alkaline) the most suitable

experimental data for T estimates are those from Otten (1984) and Féménias *et al.* (2006) based on Ti amphiboles.

The authors consider that $\ln [Ti] = (2603 / T) - 1.70$. Where [Ti] is content of Ti in amphibole expressed in atoms per formula unit. When applied, this thermometer indicates that all studied amphiboles field crystallization Temperatures (T_1) of 850-950°C (Table 4). The highest value (953°C) is given by an amphibole core from an andesite. In andesites, T_1 averages $926 \pm 14^\circ\text{C}$ and varies from 913-953°C. The thermal stability in dacites varies from 850-900°C, its average is of $886 \pm 22^\circ\text{C}$. Only three analyses are realized on amphiboles from rhyolites, they fall among the lowest values (854, 878 and 904°C).

The difference between analyses from core and rims of phenocrysts is weak and may be considered as meaningless because the discrepancy lies in the range of overall uncertainty and never exceeds 50°C. The difference in temperature estimates between andesites and dacites-rhyolites, even slight, indicates that a portion of the magma is emplaced under much hotter conditions relative to the lower temperature portion that generally occur at the shallowest part of the same magmatic chamber.

Calculated temperatures are acceptable but should be evaluated by their testing against another thermometer T_2 ; for this purpose the plagioclase + hornblende thermometer of Blundy and Holland (1990) is used:

$$T = \frac{0.677P - 48.98 + Y}{-0.0429 - 0.008314 \ln K}$$

With

$$K = \left(\frac{Si_{Ab} - 4}{8 - Si_{Ab}} \right) X_{Ab}^{Plag}$$

Where Si_{Ab} is the number of atoms per formula unit in amphiboles, P is the pressure in Kbar and T is the temperature in K, with $Y = 0$ for $X_{Ab} > 0.5$ and $Y = 8.06 + 25.5 (1 - X_{Ab})^2$ for $X_{Ab} < 0.5$. This thermometer should only be used in temperatures ranging from 500 to 1100°C and for assemblages with plagioclase less calcic than An_{92} and with amphiboles containing less than 7.8 Si atoms pfu. Studied Samples have the required conditions.

Although slightly lower the calculated crystallization temperatures T_2 (Table 3) are similar to those found using the previous thermometer. The highest values are from andesites (886-909°C) and lowest from dacites and rhyolites (805-892°C). The difference between the two calculated temperatures for the same sample is of $\pm 8^\circ$ to $\pm 61^\circ\text{C}$.

CONCLUSION

The Neogene andesitic group from Northwest Annaba (Algeria) is mainly composed of Andesites and dacites but includes a complete differentiated succession from very rare basalts to rhyolites. All these rocks are genetically related to each other (in space, time and composition). Andesites are characterized by their apparent heterogeneity and their widespread pyroclastic facies. In addition to the lack of olivine, orthopyroxene is rather restricted whereas plagioclase, clinopyroxene, hydrous minerals are abundant.

Their petrography, mineralogy and bulk rock geochemistry including $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios, major, trace and Rare Earth Elements, provide evidence that these Andesites are mostly acid, highly potassic and belong to a calc-alkaline series of active continental margin.

The microprobe analysis of the amphiboles from these andesites shows that they are calcic ($\text{Ca} > 1.5$ apfu) with low Si contents ($\text{Si} < 6.5$ apfu). They belong to two subgroups: on the one hand magnesiohastingsite, pargasite, kersutite defined by $(\text{Na} + \text{K})^A > 0.5$, on the other tschermakite with $(\text{Na} + \text{K})^A < 0.5$. Amphibole analyses conform to the relationship predicted by the tschermak substitution. The X_{Mg} ratios are within 0.5 and 1.0 making all the amphiboles magnesian.

Hornblende composition is used as thermobarometers: Al and Ti contents of Ca amphiboles allow the simultaneous assignment of crystallization pressure and temperature:

- Using two different calibration of Al in hornblende (A H barometry) pressure found are similar and averaging $5 \pm 0.5 \text{ Kb}$ which correspond to a shallow crustal chamber
- Temperatures are also calculated using Ti in hornblende geothermometer compared with two minerals (plagioclases + amphiboles) thermometer: temperature estimates vary from 800-950°C. From amphibole thermobarometry one might deduce the following:
- It is obvious that magma originating andesites should be situated at the upper parts of the mantle, or at the lower parts of the crust (70-100km deep). But later, a portion of this magma is temporarily stored and most differentiation occurs in shallow crustal chamber (10-20 km deep) which is in agreement with pressure estimate.
- Because temperature estimates are not sufficiently different from cores to rims, rare zoning observed in amphiboles and strong ones in plagioclases may be interpreted as a self organisation in convective magma chamber during long storage without any significant change in heating (L'Heureux and Jamtveit, 2002).

- The heterogeneity in the effusive style may also be explained: It is probably linked to a change in volatile contents of the magma because at this crustal level (10-20 km) and particularly during Neogene time, magma chamber should be under episodic variation of surrounding stress related to the regional tectonics.
- Andesites are mainly pyroclastic, acid and potassic: In addition to a late silicification, these features may be attributed to a long dormancy within crustal chamber that contribute to a greater differentiation and potassium richness. This salient chemical characteristic, may be due for the most part to a crustal assimilation

REFERENCES

- Allen, J.C. and A.L. Boettcher, 1978. Amphiboles in andesite and basalt: II. Stability as a function of P - T - f_{O_2} . *Am. Mineralogist*, 63: 1074-1087.
- Anderson, J.L. and D.R. Smith, 1995. The effects of temperature and f_{O_2} on the Al-in-hornblende barometer. *Am. Mineral.*, 80: 549-559.
- Arafa, M. and B. Auvray, 1986. Le magmatisme néogène du secteur Cap de Fer-Chetaibi (Nord Est algérien). 11^{ème} Réunion des Sciences de la Terre, Clermont Ferrand, Soc., Géol., Fr.2 édit. Paris, pp: 4.
- Arafa, M., 1990a. Pétrologie et géochimie des andésites de la région de L'Edough (N.E Algérie) 2^{ème} Congrès International des Sciences de la Terre, pp: 33, Tunis.
- Arafa, M., 1990b. Pétrologie et géochimie des granitoides calco-alcalins néogènes de la région de Annaba (NE Algérie), 15^{ème} Colloque de Géologie Africaine, Nancy, France, pp: 381.
- Bellon, H., 1976. Séries magmatiques néogènes et quaternaires du pourtour méditerranéen occidental, comparées dans leur cadre géochronométrique. Implications géodynamiques. Thèse d'Etat, Université Paris-Sud-Orsay, pp: 367.
- Blundy, J.D. and T.J.B. Holland, 1990. Calcic amphibole equilibria and a new amphibole-plagioclase Geothermometer. *Contrib. Mineral. Petrol.*, 104: 208-224.
- Cosca, M.A., E.J. Esson and J.R. Bowman, 1991. Complete chemical analyses of metamorphic hornblende: implications for normalization, calculated H_2O activities and thermobarometry: *Contrib. Mineral. Petrol.*, 108: 472-484.
- Deer, W.A., R.A. Howie and J. Zussman, 1965. *Rock-forming Minerals*. Longman. London, Vol.5.
- Femenias, O., J.C.C. Mercier, C. Nkono, H. Diot, T. Berza, M. Tatu and D. Demaiffe, 2006. Calcic amphibole growth and composition in calc-alkaline Magmas: Evidence from the Motru Dike Swarm (Southern Carpathians, Romania). *Am. Mineral.*, 91: 73-81.
- Gill, G.B., 1981. Orogenic andesites and plate tectonics. In: *Minerals and Rocks*, 16, Heidelberg (Ed). New York, pp: 390.
- Hilly, J., 1962. Etude géologique du massif de L'Edough et du Cap de Fer (Est Constantinois). Publications du Service de la Carte Géologique de l'Algérie (Nouvelles séries) 19: 408.
- Hollister, L.S., G.C. Grissom, E.K. Peters, H.H. Stowell and V.B. Sisson, 1987. Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons. *Am. Mineralogist*, 72: 231-239.
- Kuno, H., 1968. Origin of andesites and its bearing on the island arc structure. *Bull. Volcanol.*, 32: 141-176.
- Leake, B.E., A.R. Woolley, C.E.S. Arps, W.D. Birch, M.C. Gilbert, J.D. Grice, C. Hawthorn, A. Kato, H.J. Kisch, V.G. Krivovichev, K. Linthout, J. Laird, J. Mandarine, W.V. Maresch, E.H. Nickel, N.M.S. Rock, J.C. Schumacher, D.C. Smith, N.C.N. Stephenson, L. Ungaretti, E.J.W. Whittaker and G. Youzhi, 1997. Nomenclature of amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association Commission on new minerals and mineral names. *Mineral. Mag.*, 61: 295-321.
- L'Heureux, L. and B. Jamveit, 2002. A model of oscillatory zoning in solid solutions grown from aqueous solutions: Applications to the (Ba,Sr)SC₂>4 System. *Geochimica et Cosmochimica Acta*, 66: 417-429.
- Marignac, Ch. and J.L. Zimmermann, 1983. Ages K-Ar de l'événement hydrothermal et des intrusions associées dans le district minéralisé miocène d'Ain-Barbar (Est Constantinois, Algérie). *Mineralium Deposita*, 18: 457-567.
- Maury, R.C., S. Fourcade, C. Coulon, M. El Azzouzi, H. Bellon, A. Coutelle, A. Ouabadi, B. Semroud, M. Megartsi, J. Cotten, O. Belanteur, A. Louni-Hacini, A. Piqué, R. Capdevila, J. Hernandez and J.P. Réhault, 2000. Post-collisional Neogene magmatism of the Mediterranean Maghreb margin: A consequence of slab breakoff. *Comptes rendus de l'Académie des Sciences, Paris IIA*, 331: 159-173.
- Otten, M.T., 1984. The origin of brown hornblende in the Artssjallet gabbros and dolerites. *Contrib. Mineral. Petrol.*, 86: 185-199.
- Peccerillo, A. and S.R. Taylor, 1976. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area northern Turkey. *Contrib. Mineral. Petrol.*, 58: 63-81.
- Schmidt, M.W., 1992. Amphibole composition in tonalite as a function of pressure: An experimental calibration of the Al-in-hornblende barometer. *Contrib. Mineral. Petrol.*, 110: 304-310.