Estimation of oxygen fugacity according to amphibole chemical composition in Vash granitoid , NW Natanz(Esfahan,Iran)

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Abstract

The Vash granitoid located in west of Natanz and is a part of Urumieh-Dokhtar volcanic belt. The plutonic composition is granodiorite to tonalite. Based on microprobe analysis amphiboles of Vash is monoclinic calcic amphibole and magnesio hornblende ,probably, the biotite is annite and the chlorite is penine. The chemical features indicating low temperature (744^{0c}) low pressure (1.4kbar) and medicate to high fO2 (-14.67) . High oxygen fugacity shows which, this granitoid has been formed in oxidation conditions. This conditions adopted with magmatic granites in subduction zones. Considering this study granitic magma is met- aluminous and I-type granite that formed by crystallization of subducted slab. The magma is a melt probably formed by partial melting of the oceanic crust originated from Neothetian Central Iran. ***Key word:*** *granitoid , Vash , magnesio hornblende, met aluminous ,I-type, ,fO2*

Introduction

The Vash granitoid is located in $33^0 38$`-$38^0$-43` $51^0 45$`-$51^0 34$`oligo-micen in age [1](Fig 1). The Vash granitoid includes tonalite, granodiorite, plutons. It contain plagioclase ± amphibole ± biotite + K-feldspar + quartz which are common minerals occurring in felsic metaluminous (ASI≤1) I-type granites. Accessories include magnetite + titanomagnetite + euhedral titanite + apatite + zircon.

Analytical Equipment and Structural Formulae

Electron microprobe analyses were performed at the Iran mineral processing Research center using a Cameca SX-100 instrument, equipped with 5 wavelength-dispersive spectrometers (WDS).An accelerating voltage of 15 KV and a beam current of 20 nA were used for amphibole, with a beam size of 10 µm. Special care was taken during the calibration of the major elements; all were regularly cheeked in the course of the analyses on different standards of known composition. Structural formulae for amphibole analyses were calculated on the basis of 23 oxygen (assumed anhydrous) with site allocation as suggested by [10](Tab 1).

Amphibole Chemistry

Microprobe analyses along with structural formula for amphiboles from the Vash granitoid are shown in Table 1. Following the recommendations of Leake et al. [8,9] all the studied amphiboles are monoclinic calcic hornblendes chemically defined with respect to the standard formulae Ca_2 $(Mg,Fe^{2+})_4(Al,Fe^{3+})$ $Si_7AlO_{22}(OH)_2$ as follows [Ca(M4)+ Na(M4)] > 1.34; Na(M4) < 0.67 and Mg* >0.50. Their $(Na+K)_A$ and Ti are both always less then 0.5 atoms per formula unit (apfu), representing typical magnesio-hornblende with formulae of Ca2 $[Mg4(Al,Fe^{3+})][(Si_7Al)O_{22}](OH)_2$ which is distinct mafic mineral in I-type granites. The studied hornblendes are chemically homogeneous in composition and high in Mg*

=Mg/(Mg+Fe2+) ratios which range from 0.72-0.81 from 6.900 to 7.151 apfu, Features confirming magnesio-hornblende.

Pressure

To obtain an initial estimate of pressure independent of temperature for Vash amphiboles, the barometer of Schimidt [5] is utilized as equation1:

Ps(±0.6kbar) = -3.01 +4.76 Al(total),r_2=0.99(eq.1)

Where, P_s is pressure in kbar and Al^T is the total Al-content of hornblende in apfu. This barometer was derived from the results of experiments with tonalite and granodiorite, which were carried out within the near-solidus region at 665-700 °C under pressures of less than 13 Kbar [4]. Practical application of this barometer requires attention to several issues. In the present work, the main reason of the usage is that hornblende is texturally in equilibrium with the assemblage of biotite, quartz, plagioclase, K-feldspar, titanite and Fe-Ti oxides, that is the same mineral assemblage as for the Schmidt´s calibration (eq. 1).Using the above geobarometer, the calculated pressures for Vash amphiboles show low values (< 3 kbar) ranging from 2.97 to 0.81 kbar (Table 1)which indicate shallow depths. Table 1: Representative electron microprobe analyses and calculated structural formulae of hornblende (23 oxygen atoms) from Vash granitoid (oxides, wt%).References : PS: Schmidt (1992)[11]; TA:Holland & Blundy (1994)[7].

Temperature

To estimate the amphiboles temperature, the calculated P_s from Schmidt´s barometer (eq. 1) is substituted for the value of P in the hbld-plag thermometer of [13] Which is shown as equation 2:

$$\mathbf{T_A(\pm 40c^0)=\{-76.95+0.79P+Y_{ab}+39.4X^A{}_{Na}+22.4X^A{}_k(41.5-2.89P)X^{M2}{}_{Al}\}/\{-0.0650-RLn[(27X^A{}_{vac}*X^T{}_{si}*X^{pl}{}_{ab})/256*X^A{}_{Na}*X^T{}_{Al}]-273}$$

Where, T_A is amphibole temperature (ºC), P is pressure (kbar) calculated from equation No. 1, $X^{Pl}{}_{Ab} > 0.5$: $Y_{Ab} = 0.0$ else $Y_{Ab} = 12.0\ (1-X^{Pl}{}_{Ab})^2 - 3.0$ kJ, R = 0.0083144 $kJK^{-1}\ mol^{-1}$, and various cation X terms are summarized in Appendix 1. The average mole fraction of albite in plagioclase ($X^{Pl}{}_{Ab}$) for each sample is summarized in Table 1. This equation was calibrated for exchange equilibrium Ed +4Qtz = Tr +Ab, and is widely applied for magnesio-hornblendes when pressure is known [4, 12]. The above equation yields low temperatures (≤ 700 ºC), raging from 699 to 740 ºC (Table 1).

Oxygen Fugacity (fO_2)

To clarify the fO_2 stability of the Vash granitoud, the equilibrium expression of Wones [5] is used as the following (equation 4): **Log f O_2 = - 30930/T_A+14.98+0.142 (P_S-1)/$T_{(A)}$ (eq.4)** Where, T_A is temperature (in Kelvin's) and P_s is pressure (in bars) calculated by equation 1 and 2, respectively (table 1).The equation 4 is applied to granitoid rocks containing titanite + magnetite + quartz assemblage with amphibole comprising intermediate to high Mg^* ratios [5], The conditions are adopted for the present study. Using the equation 4, logfO_2 was calculated for Vash amphiboles and listed in Table 1. The calculated values of logfO_2 show a restricted range from -11.37 to -18.49 with an average -14.93, confirming all petrological and mineralogical context that inferred oxidation conditions for the Vash granitoid. The obtained values of logfO_2 are moderately low because of the slight incorporation of pressure, low values of P_s and T_A which are substituted in Wones' equation [5]. In particular, Wones' equation is mainly affected by T_A which is low in this work. This oxidation state is fairly similar to the typical low-pressure (2.5 kbar) and low-temperature (~700 ºC), oxidized (logfO_2 = -15) I-type granites of the LFB [6]. A plot of 10,000/T(ºk) vs. logfO_2 provides linear trend (Fig. 1E) well above the stability of FMQ (Fe_2 Sio_4 + Fe_3O_4 + Sio_2), between the NNO (Ni + NiO) and HM (Fe_2O_3 + Fe_3 O_4) buffers, a feature attributed to Oxidized, I-type granites [6a,b].Typical ilmenite-granites contain hornblende with Fe/(Fe+Mg) ratios of 0.80 to 0.99 [3] but hornblendes from this study are low in Fe/(Fe+Mg) ratios (≤0.38), suggesting early magnetite crystallization and oxidized condition. The calculated T and logfO_2 values for Vash amphiboles are essentially different from typical dry, S-type, ilmenite-granites of the LFB. Major differences include: higher temperature (>800 ºC), wider range of T (860-1026±7 ºC) and lower fO_2 (below FMQ) for S-type granites [5]. These differences are reflected from the source composition, but the availability of H_2O in I-type granites largely determines T and fO_2 conditions. In the present work, the rnge of T and p are similar to H_2O-saturated magmas of tonalite to granodiorite composition [12] in which hornblende equilibration occurs in the vicinity of the solidus (Fig. 1F).

Conclusions

The studied magnesio-hornblendes represent typical characteristics of low-temperature, low-pressure and oxidized conditions for felsic metaluminous I-type rocks of the Vash granitoid. The composition of Vash amphiboles was appropriate for utilization of principal thermo-barometers, yielding the satisfactory results of T (699-740 ºC), P (<2 kbar) and log fO_2 (-11.37 to -18.49) values. The range of calculated temperatures is essentially lower than the temperature range reported for mafic low-temperature I-type granites of Australia (700-800 ºC). This lower temperature range is consistent with the quartzofeldspathic nature of the Vash granitoid (ASI =~1) and recommends a thermal boundary of ~700ºC between mafic and felsic low-temperature I-type granites, In other words, the low-temperature I-type granites formed from magmas which crystallized in temperatures ~700 to 800 ºC for mafic composition, and ~600 to 700 ºC for felsic compositions.

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Table 1 : Electron microprobe analyses Amphiboles (Wt.%) of the sample from the granitoids of the Vash area

Sample	V.Am.4.1	V.Am.4.2	V.Am.4.3	V.Am.4.4	V.Am.4.5
SiO2	۴۷.۲۷۳	۴۸.۴۵۳	۴۷.۵۷۰	۴۸.۳۶۰	۴۶.۷۰۱
TiO2	۱.۳۵۴	۱.۰۶۵	۱.۳۵۵	۱.۴۰۵	۱.۲۱۵
Al2O3	۶.۰۳۹	۵.۵۶۰	۶.۲۸۲	۴.۹۷۳	۶.۵۴۹
FeO	۱۴.۱۲۴	۱۴.۴۹۰	۱۲.۷۸۱	۱۴.۲۲۶	۱۳.۷۸۵
MnO	۰.۵۵۵	۰.۶۱۷	۰.۳۶۷	۰.۷۲۴	۰.۴۳۹
MgO	۱۴.۳۳۹	۱۴.۱۶۸	۱۵.۲۱۰	۱۴.۵۲۵	۱۴.۸۷۹
CaO	۱۱.۱۵۵	۱۱.۲۶۴	۱۱.۴۶۵	۱۱.۶۱۹	۱۰.۹۲۳
Na2O	۱.۳۷۲	۱.۰۳۶	۱.۳۸۴	۰.۹۲۵	۱.۴۹۶
K2O	۰.۴۴۹	۰.۴۶۳	۰.۴۸۷	۰.۳۶۵	۰.۴۵۵
TSi	۶.۹۰۰	۷.۰۳۳	۶.۸۹۷	۷.۰۲۹	۶.۷۹۰
TAl	۱.۰۳۸	۰.۹۵۰	۱.۰۷۳	۰.۸۵۱	۱.۱۲۱
TFe+3	۰.۰۶۲	۰.۰۱۷	۰.۰۳۰	۰.۱۱۹	۰.۰۸۸
TTi	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
Sum-T	۸.۰۰۰	۸.۰۰۰	۸.۰۰۰	۸.۰۰۰	۸.۰۰۰
CAl	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
CFe+3	۰.۸۴۱	۰.۸۵۴	۰.۷۶۶	۰.۷۱۶	۰.۰۳۴
CTi	۰.۱۴۹	۰.۱۱۶	۰.۱۴۸	۰.۱۵۴	۰.۱۳۳
CMg	۳.۱۲۰	۳.۰۶۶	۳.۲۸۸	۳.۱۴۷	۳.۲۲۵
CFe+2	۰.۸۲۱	۰.۸۸۸	۰.۷۵۴	۰.۸۹۴	۰.۵۵۳
CMn	۰.۰۶۹	۰.۰۷۶	۰.۰۴۵	۰.۰۸۹	۰.۰۵۴
CCa	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
Sum-C	۵.۰۰۰	۵.۰۰۰	۵.۰۰۰	۵.۰۰۰	۵.۰۰۰
BMg	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
BFe+2	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
BMn	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
BCa	۱.۷۴۵	۱.۷۵۲	۱.۷۸۱	۱.۸۰۹	۱.۷۰۲
BNa	۰.۲۵۵	۰.۲۴۸	۰.۲۱۹	۰.۱۹۱	۰.۲۹۸
Sum-B	۲.۰۰۰	۲.۰۰۰	۲.۰۰۰	۲.۰۰۰	۲.۰۰۰
ACa	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰	۰.۰۰۰
ANa	۰.۱۳۳	۰.۰۴۳	۰.۱۷۰	۰.۰۷۰	۰.۱۲۳
AK	۰.۰۸۴	۰.۰۸۶	۰.۰۹۰	۰.۰۶۸	۰.۰۸۴
Sum-A	۰.۲۱۶	۰.۱۲۹	۰.۲۶۰	۰.۱۳۸	۰.۲۰۸
Sum-Cat	۱۵.۲۱۶	۱۵.۱۲۹	۱۵.۲۶۰	۱۵.۱۳۸	۱۵.۲۰۸
Sum-O	23.000	23.000	23.000	23.000	23.000
Mg*	0.79	0.77	0.81	0.77	0.85
Fe/(Fe+Mg)	0.35	0.36	0.32	0.35	0.34
$X^{Pl}_{Ab(mole)}$	0.74	0.71	0.58	0.80	0.71
Ps(kbar)	1.93	1.5	2.09	1.04	2.32
TA(C^0)	795.7	712.5	877.9	651	785
Log fo_2	-13.95	-16.40	-11.89	-18.49	-14.27

Sample	V.Am.6.1	V.Am.6.2	V.Am.6.3	V.Am.6.4	V.Am.6.5
SiO2	47.103	46.917	46.631	47.864	46.850
TiO2	0.917	1.197	1.375	0.783	0.650
Al2O3	5.415	6.142	6.344	5.16	4.619
FeO	15.607	14.027	15.697	15.139	15.427
MnO	0.798	0.171	0.416	0.729	0.553
MgO	11.255	11.152	14.381	11.110	13.812
CaO	10.304	10.955	11.064	10.680	12.331
Na2O	1.192	1.347	1.480	1.200	1.684
K2O	0.396	0.479	0.454	0.336	0.353
TSi	6.853	6.716	6.656	6.942	6.937
TAl	0.929	1.167	1.095	0.884	0.743
TFe+3	0.208	0.118	0.256	0.169	0.200
TTi	0.000	0.000	0.000	0.000	0.000
Sum-T	8.000	8.000	8.000	8.000	8.000
CAl	0.000	0.000	0.000	0.000	0.000
CFe+3	0.872	0.251	1.195	1.154	0.609
CTi	0.100	0.144	1.195	1.154	0.074
CMg	3.096	3.106	3.127	3.125	3.033
CFe+2	0.873	0.962	0.440	0.540	1.147
CMn	0.098	0.239	0.054	0.096	0.130
CCa	0.000	0.000	0.000	0.000	0.000
Sum-C	5.000	5.000	5.000	5.000	5.000
BMg	0.000	0.000	0.000	0.000	0.000
BFe+2	0.000	0.000	0.000	0.000	0.000
BMn	0.000	0.000	0.000	0.000	0.000
BCa	1.705	1.735	1.624	1.96	1.962
BNa	0.306	0.338	0.225	0.265	0.038
Sum-B	2.000	2.000	2.000	2.000	2.000
ACa	0.000	0.000	0.000	0.000	0.000
ANa	0.265	0.121	0.122	0.000	0.265
AK	0.074	0.090	0.091	0.066	0.067
Sum-A	0.339	0.211	0.137	0.066	0.333
Sum-Cat	15.339	15.211	15.193	15.065	15.333
Sum-O	23.000	23.000	23.000	23.000	23.000
Mg*	0.78	0.82	0.67	0.85	0.77
Fe/(Fe+Mg)	0.38	0.35	0.37	0.37	0.38
$X^{Pl}_{Ab(mole)}$	0.63	0.65	0.65	0.60	0.76
Ps(kbar)	1.11	2.05	2.07	1.28	1.002
TA(C^0)	781	[illegible]	[illegible]	[illegible]	[illegible]
Log fo_2	11.37	[illegible]	13.85	-14.75	13.58

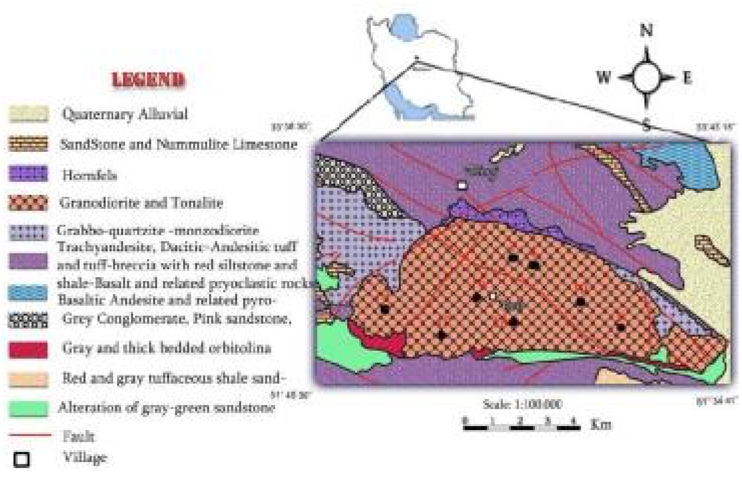

Fig1: Geological of the map of the area under study

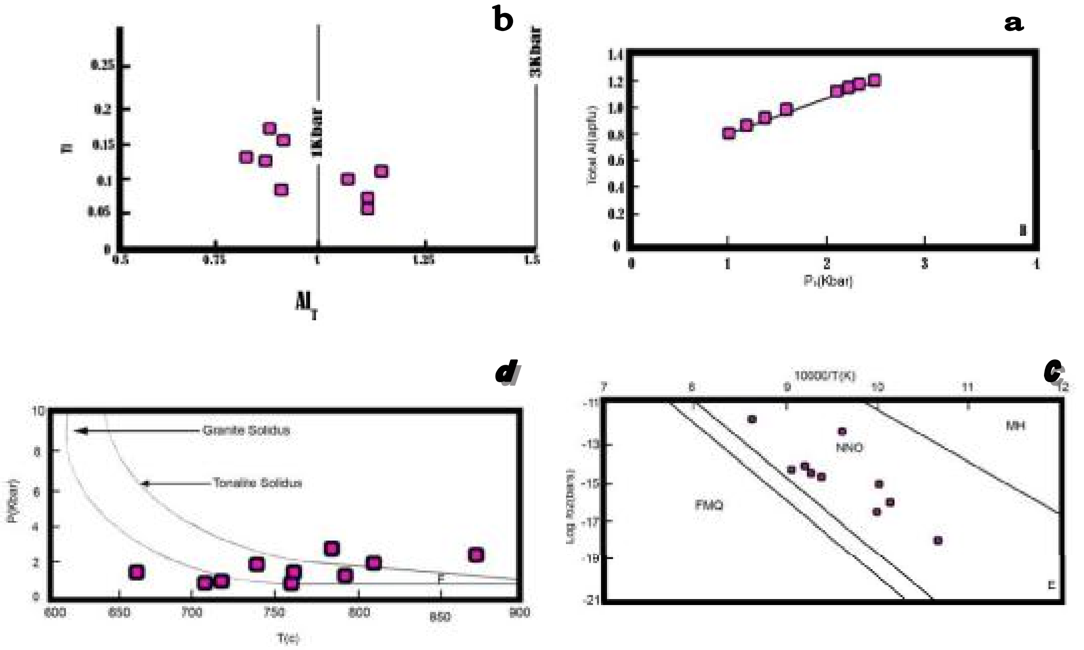

Fig 2: Compositional variation and p-T-fO_2 condition for Vash amphiboles. (A) positive correlation between calculated Ps and total Al-content of hornblende. (B) Total Al versus Ti contents with pressure contours determined according to . (C) plot of logfO_2 (bars) versus 10000/T(ºK) showing oxidation state well above the FMQ, between MH and MNO buffers, with phase boundaries after Wonse [13]. (D) Diagram showing p(kb) versus T(ºC) for Vash amphiboles which occur in the vicinity of solidus. The solidus lines are after [3].