

Thermobarometry of Ca-amphibole in a Typical Low-temperature I-type Granite from Kashmar, Iran

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Abstract

The Kashmar granitoid (42.5 Ma) occurs in NE Central Iran Plate (CIP). It mainly includes felsic metaluminous ($ASI \leq 1$) I-type granite and granodiorite plutons. Microprobe analyses show that the Kashmar amphiboles are low in Ti and $(Na+K)_A$ contents (all < 0.5 apfu), indicating magnesio-hornblende, a distinct mafic mineral of low-temperature I-type granites. Also, the content of Al_2O_3 is low, suggesting low-pressure crystallization. The Mg^* ratio is high (0.60–0.75) and the Al^{IV} is extremely low (< 0.1 apfu), but Fe^{3+} is much higher than Al^{IV} , features confirming low-pressure and low-temperature conditions. Utilizing the modern thermo-barometers, the pressures of ≤ 3 kb and average temperature of 655 °C were calculated for Kashmar amphiboles. The attributed $\log fO_2$ values are negative, ranging from -16.59 to -19.40 and plotting above the QFM stability. Results of this study propose a thermal boundary of ~700 °C between felsic (~600–700 °C) and mafic (~700–800 °C) low-temperature I-type granites, and reinforce the modern granite subdivision.

Keywords

Amphibole Chemistry, I-type, Granitoid, Low-temperature, Kashmar, Iran.

1. Introduction

The Kashmar granitoid (35°15'–35°25' N and 58°15'–58°55' E) is Middle Eocene (42.5 Ma) in age [1] and the largest plutonic mass (~200 km²) occurring in the Taknar Zone. It intrudes into andesitic lavas and pyroclastic rocks of Eocene age (Fig. 1). The Kashmar granitoid includes tonalite, granodiorite, granite and alkali feldspar granite plutons. Among these, granodiorite and granite are dominant and constitute ~90% of the granitoid exposure. They contain metaluminous rocks and minerals ($ASI \leq 1$), indicating I-type characteristic. Field, petrography and geochemical data precisely suggest a 'simple suite' for the Kashmar granitoid. Based on the modern nomenclature of granites, the *simple suite* corresponds fairly close to the low-temperature I-type granites. Because amphibole is one of the early minerals crystallizing in most granite melts, and is also sensitive to physiochemical states of magma, the present study approaches amphibole chemistry with an attempt to:

(a) determine P , T , fO_2 and the composition of Kashmar amphiboles; (b) verify the geological interpretations dealing with low-temperature feature; (c) propose a thermal boundary between felsic and mafic low-temperature I-type granites.

2. Equipment and Structural Formula

Electron microprobe analyses were performed at the Macquarie University, Australia using a Cameca SX-50 instrument, equipped with 5 wavelength-dispersive spectrometers. Structural

formulas were calculated on the basis of 23 oxygen (assumed anhydrous) with site allocation as suggested by [2]. The Fe^{3+} content was estimated by utilizing assumptions of crystal-chemical limitations on cation substitution and total cation assumptions as outlined by [2]. In this case the predominant option used was total cations exclusive of Ca, Na and K calculated to 13 (13eCNK) with all Fe as FeO contents. This succeeded in successful atomic formula for all analyses. The content of Al^{IV} was calculated as the difference between full tetrahedral occupancy (8.0 cations) and the number of Si cations. Amphibole nomenclature and site allocation follow the recommendations of [3, 4]. Calculation of mole fractions and assignment of site occupancies are summarized in Appendix 1.

3. Composition of Kashmar Amphibole

The analyzed amphiboles (Table 1) are monoclinic calcic hornblendes, chemically defined with respect to the standard formula $Ca_2(Mg,Fe^{2+})_4(Al,Fe^{3+})Si_7AlO_{22}(OH)_2$ 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 than 0.5 atoms per formula unit (apfu), representing typical magnesio-hornblende with the following formula:

$Ca_2[Mg_4(Al,Fe^{3+})][(Si_7Al)O_{22}](OH)_2$ which is distinct mafic mineral in I-type granites. They are homogeneous in composition, high in $Mg^* = Mg/(Mg + Fe^{2+})$ ratios (0.60 – 0.75) and intermediate in Si (6.800–7.155) values, confirming magnesio-hornblende.

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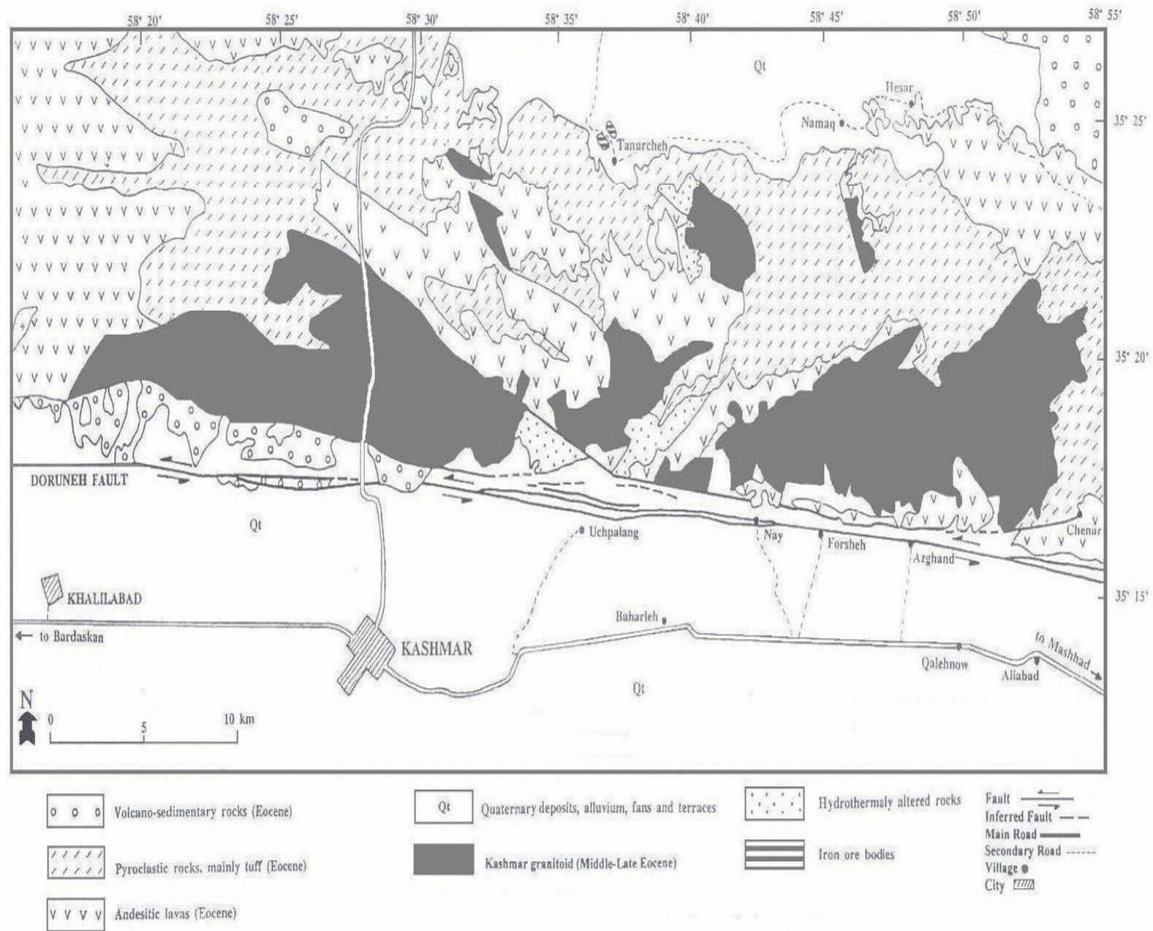


Figure 1. Geological map of Kashmar area, northeastern Central Iran Plate.

| Appendix 1. Calculation of mole fractions and assignment of site occupancies for Kashmar amphiboles | |
|---|---|
| Amphibole: | |
| ^{28}Si | = Si-4.0 |
| ^{27}Al | = 8.0-Si |
| ^{48}Ti | = Ti |
| ^{40}Al | = Al+Si-8.0 |
| $^{56}\text{Fe}^{2+}$ | = Fe^{2+} (if any) |
| ^{56}Fe | = $[2 \cdot (^{40}\text{Al} + ^{48}\text{Ti} + ^{56}\text{Fe}^{2+})] \cdot \text{Fe} / (\text{Fe} + \text{Mg})$ |
| ^{24}Mg | = $[2 \cdot (^{40}\text{Al} + ^{48}\text{Ti} + ^{56}\text{Fe}^{2+})] \cdot \text{Mg} / (\text{Fe} + \text{Mg})$ |
| $^{\text{Na}}$ | = $(\text{Si} + \text{Al} + \text{Ti} + \text{Fe}^{2+} + \text{Mg} + \text{Fe} + \text{Mn} + \text{Ca} + \text{Na}) - 15$ |
| A_1 | = $1 - ^{\text{Na}} - \text{K}$ |
| X_{Si}^{28} | = $^{28}\text{Si} / 4.0$ |
| X_{Al}^{27} | = $^{27}\text{Al} / 4.0$ |
| X_{Al}^{40} | = $^{40}\text{Al} / 2.0$ |
| X_{Mg}^{24} | = $^{24}\text{Mg} / 2.0$ |
| X_{Fe}^{56} | = $^{56}\text{Fe} / 2.0$ |
| $X_{\text{Na}}^{\text{Na}}$ | = $^{\text{Na}}$ |
| X_{K}^{K} | = K |
| X_{V}^{V} | = refers to the alkali site vacancy. |
| Plagioclase: | |
| $X_{\text{Na}}^{\text{Na}}$ | = $\text{Na} / (\text{Ca} + \text{Na} + \text{K})$ |
| The average mole fraction of albite in plagioclase ($X_{\text{Na}}^{\text{Na}}$) is always > 0.50 $\rightarrow Y_{\text{Al}} = 0$ | |
| The $X_{\text{Na}}^{\text{Na}}$ value for each sample is summarized in Table 1. | |
| Note: 1) 13eCNK means the normalizing of the cations to the $(13)^{\text{Ox}} - \text{Ca} - \text{Na} - \text{K}$ value on the presumption that Fe^{2+} , Mg, and Mn do not occupy (M4); 2) The ratios $\text{Fe}^{2+} / (\text{Fe}^{2+} + \text{Fe}^{3+})$ and $\text{Fe}^{3+} / (\text{Fe}^{2+} + \text{Fe}^{3+})$ were calculated for each amphibole by the 13eCNK method; examples are listed in Table 1; 3) All cations are in atoms per formula unit (apfu); 4) The source of plagioclase analyses is [1]. | |

The analyzed hornblendes (Table 1) are low in Al_2O_3 (4.67 to 7.17 wt%), Na_2O (1.01 to 1.44 wt%) and TiO_2 (1 to 1.75 wt%) contents, chemical characteristics indicating low pressure, low temperature and high $f\text{O}_2$ states, respectively. The Al^{VI} is low (< 0.1 apfu) but Fe^{3+} is about ten times higher than Al^{VI} . These features plus intermediate Si contents of Kashmar amphiboles suggest no Tschermaks and edenite substitutions, possibly because Ca-amphiboles crystallized in low pressures from shallow level intrusions [5, 6]. The MgO/FeO ratio is low (mostly < 1), indicating that hornblende crystallized from a felsic melt [7]. The Mg and Fe contents of Kashmar amphiboles are distinct and appropriate for Al-in-hornblende barometry because they have $0.4 \leq \text{Fe}^{\text{tot}} / (\text{Fe}^{\text{tot}} + \text{Mg}) < 0.65$ and $0.2 < \text{Fe}^{3+} / (\text{Fe}^{3+} + \text{Fe}^{2+})$, the limits established by [8, 9], where Mg and Fe are calculated by the 13eCNK method.

Table1. Representative electron microprobe analyses and calculated structural formula of hornblende (23 oxygen atoms) from Kashmar granitoid (oxides, wt%). Grd = Granodiorite; R = Rim; C = Core

| Sample No. | R15908 | R15908 | R15910 | R15910 | R15918 | R15918 | R15909 | R15909 |
|---------------------------------------|--------|--------|---------|---------|---------|---------|---------|---------|
| Rock Name | Grd. | Grd. | Granite | Granite | Granite | Granite | Granite | Granite |
| Rock ASI | 0.92 | 0.92 | 0.87 | 0.87 | 0.99 | 0.99 | 0.99 | 0.99 |
| Spot | 1-R | 1-C | 2-R | 2-C | 2-R | 2-C | 1-R | 1-C |
| SiO ₂ | 47.43 | 45.71 | 48.45 | 49.20 | 46.58 | 45.85 | 47.18 | 48.97 |
| TiO ₂ | 1.32 | 1.75 | 1.23 | 1.00 | 1.12 | 1.59 | 1.09 | 1.11 |
| Al ₂ O ₃ | 6.51 | 7.17 | 5.51 | 5.08 | 6.49 | 7.12 | 5.74 | 4.67 |
| MgO | 12.35 | 11.17 | 14.23 | 14.42 | 10.59 | 10.45 | 12.62 | 13.74 |
| CaO | 10.81 | 11.21 | 11.41 | 11.14 | 10.79 | 10.88 | 11.03 | 10.83 |
| MnO | 0.69 | 0.68 | 0.45 | 0.55 | 0.88 | 0.69 | 0.85 | 0.88 |
| FeO | 16.71 | 17.56 | 14.00 | 13.85 | 18.83 | 18.53 | 16.41 | 14.90 |
| Na ₂ O | 1.16 | 1.43 | 1.19 | 1.10 | 1.01 | 1.15 | 1.44 | 1.17 |
| K ₂ O | 0.58 | 0.76 | 0.45 | 0.50 | 0.69 | 0.81 | 0.57 | 0.51 |
| Total | 97.56 | 97.44 | 97.01 | 96.84 | 96.98 | 97.07 | 96.93 | 96.78 |
| Si | 6.924 | 6.800 | 7.064 | 7.147 | 6.933 | 6.843 | 6.968 | 7.155 |
| Ti | 0.144 | 0.196 | 0.135 | 0.109 | 0.126 | 0.179 | 0.121 | 0.122 |
| Al | 1.120 | 1.257 | 0.946 | 0.870 | 1.138 | 1.253 | 1.000 | 0.803 |
| Mg | 2.687 | 2.476 | 3.092 | 3.123 | 2.349 | 2.326 | 2.779 | 2.991 |
| Ca | 1.690 | 1.787 | 1.782 | 1.733 | 1.722 | 1.740 | 1.745 | 1.695 |
| Mn | 0.085 | 0.085 | 0.055 | 0.068 | 0.111 | 0.087 | 0.107 | 0.108 |
| Fe | 2.039 | 2.185 | 1.707 | 1.683 | 2.344 | 2.312 | 2.026 | 1.821 |
| Na | 0.329 | 0.412 | 0.335 | 0.309 | 0.292 | 0.333 | 0.410 | 0.331 |
| K | 0.107 | 0.114 | 0.101 | 0.093 | 0.130 | 0.154 | 0.110 | 0.095 |
| Total | 15.125 | 15.342 | 15.217 | 15.135 | 15.145 | 15.227 | 15.266 | 15.121 |
| Al ^{IV} | 1.076 | 1.200 | 0.936 | 0.853 | 1.067 | 1.157 | 1.000 | 0.803 |
| Al ^{VI} | 0.044 | 0.057 | 0.010 | 0.017 | 0.071 | 0.096 | 0.000 | 0.000 |
| Fe ³⁺ | 0.930 | 0.623 | 0.658 | 0.748 | 0.876 | 0.736 | 0.810 | 0.827 |
| Fe ²⁺ | 1.109 | 1.562 | 1.049 | 0.935 | 1.468 | 1.576 | 1.216 | 1.994 |
| Ca(M3) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe(M4) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ca(M4) | 1.690 | 1.787 | 1.782 | 1.733 | 1.722 | 1.740 | 1.745 | 1.695 |
| Na(M4) | 0.310 | 0.213 | 0.218 | 0.267 | 0.278 | 0.260 | 0.255 | 0.305 |
| Na(A) | 0.019 | 0.199 | 0.117 | 0.042 | 0.014 | 0.073 | 0.155 | 0.026 |
| K(A) | 0.107 | 0.144 | 0.101 | 0.093 | 0.130 | 0.154 | 0.110 | 0.095 |
| Mg* | 0.71 | 0.61 | 0.75 | 0.75 | 0.62 | 0.60 | 0.70 | 0.75 |
| Fe/(Fe+Mg) | 0.43 | 0.47 | 0.36 | 0.35 | 0.50 | 0.50 | 0.42 | 0.40 |
| Fe ³⁺ /Fe ^{total} | 0.46 | 0.29 | 0.39 | 0.44 | 0.37 | 0.32 | 0.40 | 0.45 |
| MgO/FeO | 0.74 | 0.64 | 1.02 | 1.04 | 0.56 | 0.56 | 0.77 | 0.92 |
| X _{Ab} ^{PI} (mole) | 0.65 | 0.65 | 0.64 | 0.64 | 0.66 | 0.66 | 0.62 | 0.62 |
| P _s (kbar) | 2.32 | 2.97 | 1.49 | 1.13 | 2.41 | 2.95 | 1.75 | 0.81 |
| P _{AS} (kbar) | 2.51 | 3.21 | 1.31 | 1.25 | 2.60 | 2.91 | 1.72 | 0.91 |
| T _A (°C) | 617 | 621 | 700 | 627 | 633 | 680 | 680 | 642 |
| log fO ₂ | -19.40 | -19.15 | -16.59 | -19.21 | -19.16 | -17.04 | -17.22 | -18.69 |

The analyzed hornblendes (Table 1) are low in Al₂O₃ (4.67 to 7.17 wt%), Na₂O (1.01 to 1.44 wt%) and TiO₂ (1 to 1.75 wt%) contents, chemical characteristics indicating low pressure, low temperature and high *f*O₂ states, respectively. The Al^{VI} is low (< 0.1 apfu) but Fe³⁺ is about ten times higher than Al^{VI}. These features plus intermediate Si contents of Kashmar amphiboles suggest no Tschermaks and edenite substitutions, possibly because Ca–amphiboles crystallized in low pressures from shallow level intrusions [5, 6]. The MgO/FeO ratio is low (mostly < 1), indicating that hornblende crystallized from a felsic melt [7]. The Mg and Fe contents of Kashmar amphiboles are distinct and appropriate for Al–in–hornblende barometry because they have 0.4 ≤ Fe^{tot}/(Fe^{tot} + Mg) < 0.65 and 0.2 < Fe³⁺/(Fe³⁺ + Fe²⁺), the limits established by [8, 9], where Mg and Fe are calculated by the 13cCNK method.

4. Pressure Determination

To obtain an initial estimate of pressure independent of temperature, the Schmidt's barometer [9] is utilized as equation No. 1 (Table 2) where, *P_S* is pressure in kbar and Al^T is the total Al–in–hornblende (apfu). The main reason of the usage of equation 1 is that hornblende is texturally in equilibrium with biotite, quartz, plagioclase, K-feldspar, titanite and Fe-Ti oxides. This mineral assemblage is the same as was applied for the Schmidt's calibration [10, 11]. The equation No.1 provides low pressures (< 3 kbar) ranging from 2.97 to 0.81 kbar for the Kashmar amphiboles (Table 1). The low pressure feature and contrary trend between Fe/(Fe + Mg) and Mg* ratios (Fig. 2A) are consistent with the presence of euhedral magnetite and titanite as early mineral phases in oxidized condition [7, 11, 12]. The

calculated *P_S* exhibit a positive correlation with Al^T (Fig. 2B). This normal trend is expected because according to several experimental studies, this range of pressure for water–saturated granites is approximately independent of temperature [9]. The estimated pressures exhibit polybaric crystallization when Al^T plots versus Ti contents (Fig. 2C).

5. Amphibole Thermometry

The calculated pressure (*P_S*) from Schmidt's barometer (eq. 1) is substituted for the value of *P* in the *hbld-plag* thermometer of Holland and Blundy [13] which is shown as equation No. 2 in Table 2 where *T_A* is amphibole temperature (°C), *P* is pressure (kbar) calculated from equation No. 1, *X^{Pl_{Ab}}* > 0.5: *Y_{Ab}* = 0.0 or else *Y_{Ab}* = 12.0 (1–*X^{Pl_{Ab}}*)² – 3.0 kJ, *R* = 0.0083144 kJK⁻¹mol⁻¹, and various cation *X* terms are summarized in Appendix 1. The equation No. 2 yields low temperatures (≤ 700 °C) which range from 617 to 700 °C (Table 1). The calculated *T_A* represents a mean value of 650 °C which is in the vicinity of H₂O–saturated granite solidus at low pressures (2 to 2.5 kbar) for felsic compositions [14–15]. The range of calculated *T_A* is within the range of water–rich felsic I–type magnetite–granites [e.g. 15] which formed in low temperatures (620–722 ± 7 °C). The calculated *T_A* represents a lower temperature for Kashmar granitoid, compared with mafic low–temperature (700–800 °C) I–type granites of Lachlan Fold Belt (LFB), Australia [16a,b]. This comparison leads to propose a thermal boundary of ~700 °C between mafic and felsic low–temperature I–type granites.

Table 2. The hornblende geothermobarometers, were used for the Kashmar amphiboles.

| Equation No. | Hornblende Geothermobarometry |
|--------------|--|
| 1 | $P_S (\pm 0.6) = -3.01 + 4.76 Al^T, r^2 = 0.99$ |
| 2 | $T_A (\pm 40 \text{ }^\circ\text{C}) = \frac{-76.95 + 0.79P + Y_{Ab} + 39.4X_{B}^{Al} + 22.4X_{K}^{Al} + (41.5 - 2.89P)X_{Al}^{Al}}{-0.0650 - R \cdot \ln [(27X_{Si}^{Al} \cdot X_{Si}^{Pl_{Ab}}) / (256X_{B}^{Al} \cdot X_{Al}^{Al})]} - 273$ |
| 3 | $P_{Al} (\pm 0.6 \text{ kbar}) = 4.76Al^T - 3.01 - \{[T - 675]/85\} \times \{0.530Al^T + 0.005294[T - 675]\}$ |
| 4 | $\log fO_2 = -30930/T_A + 14.98 + 0.142 (P_S - 1)/T_A$ |

Note: Equation references: 1–[9]; 2–[13]; 3–[8]; 4–[12].

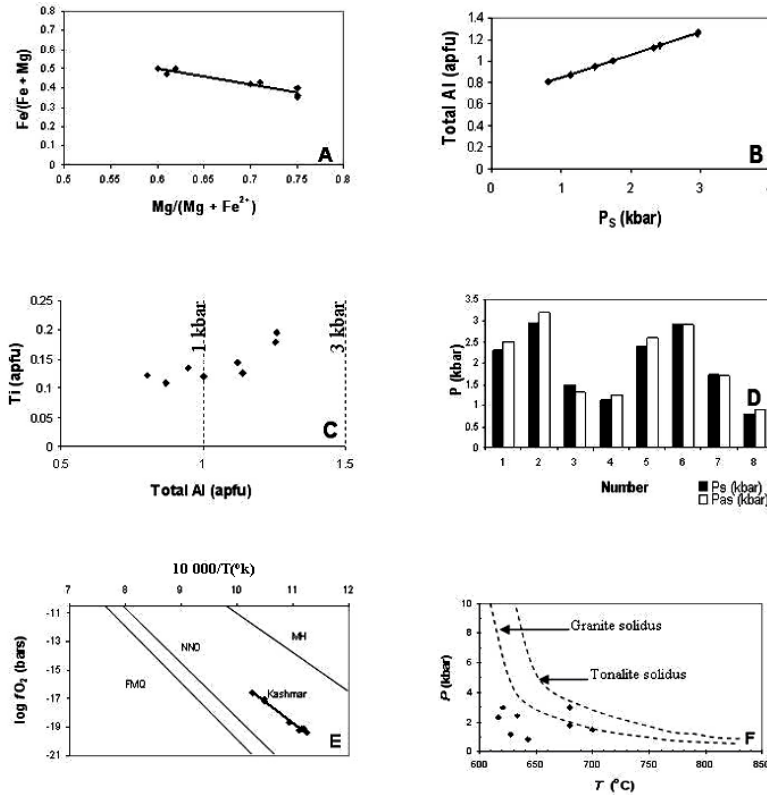


Figure 2. Compositional variation and P - T - fO_2 conditions for Kashmar amphiboles. (A): Contrary trend between Mg^* and $Fe/(Fe + Mg)$ ratios; (B): Positive correlation between calculated P_s and total Al-content of hornblende; (C): Total Al versus Ti contents with pressure contours determined according to [6]; (D): Similarity between calculated P_s (independent of temperature) and the revised estimated pressures (P_{AS}); (E): Plot of $\log fO_2$ (bars) versus $10000/T(^{\circ}K)$ showing oxidation state well above the FMQ, between MH and NNO buffers, with phase boundaries after [12]; (F): Diagram showing P (kbar) versus $T(^{\circ}C)$ for Kashmar amphiboles which occur in the vicinity of solidus. The solidus lines are after [17].

6. Pressure Revised

To obtain a revised estimate of pressure of crystallization for amphibole from plutonic rocks, using experimental data at $\sim 675^{\circ}C$ [9] and at $\sim 760^{\circ}C$ [6], Anderson and Smith [8] generated the temperature-dependent barometer which is shown as *equation* No. 3 in Table 2, where $T(^{\circ}C)$ calculated from *equation* 2 and Al^T is total Al-in-hornblende. The *equation* No. 3 yields revised estimated pressures (P_{AS}) which are very similar to P_s values specified by *equation* 1 (Table 2). For any given sample, P_{AS} is less

or more by a little amount (≤ 0.2 kbar) than P_s , indicating the reliability of the calculated P - T data (Fig. 2D). The consistency of P data can be resulted from several issues including 1) appropriately chosen thermo-barometers; 2) little or no incorporation of the temperature correction in P_{AS} determination because the average T data is inside the Schmidt's calibration [9]; 3) the extent of the temperature correction decreases with albite content of plagioclase [14] and hence, is least because average mole fraction of albite in plagioclase is high (all $X_{Ab}^{Pl} > 0.50$ moles $\rightarrow Y_{Ab} = 0$); 4) the

Mg and Fe contents of Kashmar amphiboles are within the limits established by [8, 9, 14] for P - T determination using thermo-barometer of [13].

7. Oxygen Fugacity (fO_2)

To clarify the fO_2 stability of the Kashmar granitoid, the equilibrium expression of Wones [12] is used as the *equation* No. 4, shown in Table 2 where T_A is temperature ($^{\circ}K$) and P_s is pressure (bars) calculated by *equations* 1 and 2, respectively. The calculated values of $\log fO_2$ show a restricted range from -19.40 to -16.59 with an average of -18.31 , confirming petrological and mineralogical context that inferred oxidation conditions for Kashmar granitoid. This oxidation state is fairly similar to the typical low-pressure (2.5 kbar) and low-temperature ($\sim 700^{\circ}C$), oxidized ($\log fO_2 = -15$) I-type granites of the LFB [15]. A plot of $10,000/T(^{\circ}K)$ vs. $\log fO_2$ provides linear trend (Fig. 2E) well above the QFM stability (between NNO and MH buffers), a feature attributed to oxidized I-type granites [16a,b]. The availability of H_2O in I-type granites largely determines T and fO_2 conditions. In the present work, variation in P , T and fugacity data for Kashmar amphiboles are similar to amphiboles from H_2O -saturated magmas of tonalite to granodiorite composition [14, 17–21] in which hornblende equilibration occurs in the vicinity of the solidus (Fig. 2F).

8. Conclusions

The composition of Kashmar amphiboles is appropriate for utilization of principal thermo-barometers, yielding the satisfactory results of T (617–700 °C), P (≤ 3 kbar) and $\log fO_2$ values (–16.59 to –19.40). These results are consistent with quartzofeldspathic nature ($ASI \approx 1$) and major geochemical features which indicate that the Kashmar granitoid formed under low temperature, low pressure and oxidized conditions from I-type source rocks. The range of calculated temperatures is essentially lower than the temperature range reported for mafic low-temperature (700–800 °C) I-type granites of the Lachlan Fold Belt, Australia. This lower temperature range recommends a thermal boundary of ~700 °C 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 °C for mafic compositions, and ~600 to 700 °C for felsic compositions.

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