ترکیب شیمیایی آمفیبول در گرانيتهای نوع-I با دمای پایین از منطقه کاشمر شمال شرقی ایران مرکزی

ابوالفضل سلطاوی

گروه عمران دانشگاه فنی و مهندسی، دانشگاه تربیت دبیر شهید، رحیمی، تهران

abolfazl36@hotmail.com

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چکیده: گرانيتوند کاشمر (Ma (4/3-6/5 مایا) به وسیعی از ناحیه ماگما تا کاسپیان) از نظر محاسبه طبق مطالعات میکروسکوپی و آلیزهای الکترون ماکرویروپ، آمفیبولهای کاشمر‌های از نوع مونولیتنیک کلسیک هوریستنس هستند. این کاتیون، شاخص عمده در شناخت گرانيتهای نوع-I می‌باشد. ترکیب شیمیایی آمفیبول با دمای پایین از منطقه کاشمر (Ma ۶۵ تا ۶۰ مایا) می‌باشد. سایر آنزیم‌ها از دیگر کاتیون‌ها شامل Ca, Mg, Al, Ti و Fe بوده و با توجه به ترکیب شیمیایی آمفیبول با دمای پایین از منطقه کاشمر، گرانيتهای نوع-I با دمای پایین، می‌توان یک مرز حرارتی (100-400) در دمای پایین تا دمای پایین، در سایر کتیون‌ها می‌باشد.

واژه‌های کلیدی: کلسیک آمفیبول، مونولیتنیک، گرانيتوند، کاشمر، نوع-I، دمای پایین، ایران مرکزی.
Amphibole Chemistry in Low–temperature I–type Granites from Kashmar Area, Northeastern Central Iran Plate (CIP)

Abolfazl Soltani
Faculty of Civil Engineering, Shahid Rajaee Teacher Training University, Tehran, IRAN
Email: abolfazl36@hotmail.com

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Abstract: The Kashmar granitoid (43.5–42.4 Ma) forms an extensive part of iron–oxide type magmatic belt in northern side of the Doruneh Fault. It includes plutons of tonalite, granodiorite, granite and alkali feldspar granite which are metaluminous (ASI < 1) in nature. They contain dominantly felsic minerals, representing I–type granites with low–temperature and low–pressure characteristics. According to microscopic studies and electron microprobe analyses, all amphiboles in Kashmar are monoclinic calcic hornblende which is common mafic mineral in distinction of I–type granites. The calculated structural formula for Kashmar amphiboles show characteristics of magnesio-hornblende as follow:

\[ \text{Ca(M4) + Na(M4)} > 1.34, \text{Na(M4)} < 0.67, \text{Mg}^+ > 0.50, (\text{Na + K}) \text{A} < 0.50, \text{Ti} < 0.50 \text{apfu.} \]

They are low in Al_2O_3 and TiO_2, high in Mg^+ (0.6–0.75), extremely low in Al_VI (<0.1 apfu) but significantly higher in Fe^{3+}, features indicating low temperature, low pressure and oxidized conditions. Using appropriate thermo barometers for Kashmar amphiboles, average temperature of 650 °C, pressures of ≤ 3 kb and log_{fO_2} = −16.59 to −19.40 were calculated. These results define a thermal boundary of ~700 °C between felsic and mafic low–temperature I–type granites.

Keywords: Calcic amphibole, Magnesio–hornblende, granitoid, Kashmar, I–type, Low–temperature, Central Iran.
Introduction
Recently, new and conclusive information provided by B. W. Chappell and his Co-workers has led to a fundamental subdivision of I–type granites into two groups, formed at high– and low–temperatures. The subdivision was deduced specifically from the criteria of zircon age inheritance and whole–rock geochemistry of Lachlan Fold Belt (LFB) I–type granites. The whole–rock emphasizes the concentration of REE, Zr, P, Ba, Rb and their pattern of variation in Harker plots. However, in some cases high– and low–temperature I–type granites are similar in whole–rock composition and distinction between them needs another criterion. Since amphibole is one of the early mineral 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 effects of P, T, and fO₂ on the composition of Kashmar amphiboles; (b) verify the petrochemical indications dealing with low–temperature and low–pressure features of Kashmar granitoid; (c) specify P, T, and fO₂ values of Kashmar amphiboles; (d) reinforce the subdivision of I–type granites into high– and low–temperatures; and (e) define a thermal boundary between felsic and mafic low–temperature I–type granites.

Kashmar Granitoid
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 subvolcanic mass (~200 km²) occurring in the Taknar Zone, NE Central Iran Plate (CIP). It intrudes into andesite lavas and pyroclastic rocks (mainly tuff) of Early Eocene times. The granitoid and volcanic rocks are associated with iron–oxide deposits, and form the central part of the ‘North Doruneh Fault Magmatic Belt’ that runs from the northern to eastern margins of the CIP. The Kashmar granitoid includes tonalite, granodiorite, granite and alkali feldspar granite plutons. Among these, granodiorite and granite are dominant and constitute approximately 90% of the granitoid exposure. They 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 ± ilmenite. Field, petrography and geochemical data from different plutons of the Kashmar granitoid share distinctive properties which reflect similar features of their source rocks. Such feature precisely suggests a ‘simple suite’ for the Kashmar granitoid. Base on the modern nomenclature of granites, the simple suite corresponds fairly close to the low–temperature I–type granites.

Analytical Equipment and Structural Formulae
Electron microprobe analyses were performed at the School of Earth Sciences, Macquarie University, Australia using a Cameca SX–50
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 checked 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 [2].

Ferric iron (Fe$^{3+}$) contents were estimated by utilizing assumptions of crystal-chemical limitations on cation substitution and total cation assumptions as outlined by [2]. Due to anhydrous condition, all Fe was assumed as FeO content. The Al$^{IV}$ was calculated as the difference between full tetrahedral occupancy (8.0 cations) and the number of Si cations. Amphibole nomenclature follows the recommendations of [3, 4]. Calculation of mole fractions and assignment of site occupancies are summarized in Appendix 1.

**Amphibole Chemistry**

Microprobe analyses along with structural formula for amphiboles from the Kashmar granitoid are shown in Table 1. Following the recommendations of Leake et al. [3, 4] all the studied amphiboles are monoclinic calcic hornblends chemically defined with respect to the standard formulae Ca$_2$(Mg,Fe$^{2+}$)$_4$(Al,Fe$^{3+}$)Si$_7$AlO$_{22}$(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 formulae of Ca$_2$[(Mg$_4$(Al,Fe$^{3+}$))((Si$_7$Al)O$_{22}$)](OH)$_2$ which is distinct mafic mineral in I-type granites. The studied hornblends are chemically homogeneous in composition and high in Mg$^*$ = Mg/(Mg+Fe$^{2+}$) ratios which range from 0.60 to 0.75. Their total Si varies from 6.80 to 7.155 apfu, features confirming magnesio–hornblende.

The analyzed hornblends are characteristically low in Al$_2$O$_3$ (4.67 to 7.17 wt%, Al$^V$ < 1.3 apfu), Na$_2$O (1.01 to 1.44 wt%, Na < 0.45 apfu) and TiO$_2$ contents (1 to 1.75 wt%, Ti < 0.2 apfu), the chemical parameters indicating for low-pressure, low-temperature and high-fO$_2$ states, respectively. In particular, their Si contents (6.80 to 7.16 apfu) fall within the middle range of Si values (6.50 < Si < 7.25) specified for magnesio-hornblende by the International Mineralogical Association (IMA). This mid range positioning and the extremely higher contents of ferric iron (Fe$^{3+}$ > Al$^{IV}$) suggest no Tschermaks and edenite substitutions, respectively [3, 4]. Octahedral Al (Al$^{IV}$) is less than 0.1 apfu and Fe$^{3+}$ is about ten times higher than Al$^{IV}$, again representing typical features of low-pressure calcic hornblende from shallow level intrusions [5, 6].

The contents of FeO (13.85 to 18.83 wt%) and MgO (10.45 to 14.42 wt%) are relatively high, whereas the MgO/FeO ratio is low (0.56 to 1.04,
mostly < 1), indicating hornblende crystallized from a felsic melt [7].
Variation between FeO and MgO contents in hornblende depends on fO$_2$
which can be assessed by Mg* values. In the present work, the Mg* values
for all hornblende analyses are high, supporting low–pressure and high–fO$_2$
conditions [5, 7]. Because at higher fO$_2$, magnetite precipitates and lowers
the activity of FeO in the melt, consequently hornblende crystallizes with a
high Mg* values that can be seen in granite samples (Mg* up to 0.75) which
contain higher modal contents of opaque minerals (e.g. R15910, modal Fe–
Ti oxide = 3.2 wt%). The Mg and Fe contents of Kashmar amphiboles are
distinct and appropriate for Al–in–hornblende barometry as they have
Fe$^{3+}$/Fe$^{3+}$ + Fe$^{2+}$ > 0.2 and 0.4 ≤ Fe$^{tot}$/Fe$^{tot}$ + Mg < 0.65, the limits
established by [8, 9].

**Pressure**

To obtain an initial estimate of pressure independent of temperature for
Kashmar amphiboles, the barometer of Schmidt [9] is utilized as equation 1:

$$ P_S (\pm 0.6) = 3.01 + 4.76A^{1T}, r^2 = 0.99 \text{(eq.1)} $$

where, $P_S$ is pressure in kbar and $A^{1T}$ is the total Al-content of hornblende in
apfu. This barometer was derived from the results of experiments with
tonalite and granodiorite, which where carried out within the near–solidus
region at 655–700 °C under pressures of less than 13 kbar [10]. 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 Kashmar
amphiboles show low values (< 3 kbar) ranging from 2.97 to 0.81 kbar
(Table 1) which indicate shallow depths. This range of pressure is similar to
those of hornblendes from low–Al population which yielded a significant
low pressure (< 3 kbar at 620 to 760 °C) for any plausible temperatures,
carried out by [8, 11]. The estimated pressures are confirmed by high Mg*$
(> 0.50) and low Fe/(Fe + Mg) ratios (≤ 0.50) that are observed in the
Kashmar hornblendes (Table 1). The contrary trend between Mg* and Fe/(Fe
+ Mg) ratios (Fig. 1A), together with low–pressure feature is related to early
crystallization of magnetite and titanite. The occurrence of euhedral titanite
and magnetite as early mineral phases in these rocks indicates that the
magma was relatively oxidized. In such conditions hornblende crystallizes
with low Fe/(Fe + Mg) and high Mg* ratios. The higher the Mg* value in the
hornblende, the more oxidized was the magma [7, 12].
The calculated $P_S$ exhibit a positive correlation with $Al^T$ (Fig. 1B). This normal trend is to be expected because according to several experimental studies, this range of pressure for water–saturated granites is approximately independent of temperature [9]. The estimated pressures are consistent with the geobarometer of [6] when $Al^T$ plots versus Ti contents (Fig. 1C). The range of indicated pressures, record polybaric crystallization of magma during ascent through the crust.

Table 1 Representative electron microprobe analyses and calculated structural formulae of hornblende (23 oxygen atoms) from Kashmar granitoid (oxides, wt%). Grd = Granodiorite; R = Rim; C = Core; References: Ps: Schmidt (1992); TA: Holland & Blundy (1994); PAS: Anderson & Smith (1995).
Temperature

To estimate the amphibole temperature, the calculated $P_S$ from Schmidt’s barometer (eq. 1) is substituted for the value of $P$ in the hbl–plg thermometer of [13] which is shown as equation 2:

$$T_A \left(\pm 40 ^\circ C\right) = \frac{-76.95 + 0.79P + Y_{Ab} + 39.4X_{Na} A + 22.4X_K A + (41.5 - 2.89P)X_M^2Al}{-0.0650 - R \ln \left[ \frac{27X_A X_{Pl} X_{Sl} X_{Ab} - 256X_{Na} X_{Pl}^2}{27X_A X_{Pl} X_{Sl} X_{Ab}} \right] } - 273 \text{(eq. 2)}$$

where, $T_A$ is amphibole temperature ($^\circ C$), $P$ is pressure (kbar) calculated from equation No. 1, $X_{Pl}^2 > 0.5$: $Y_{Ab} = 0.0$ or else $Y_{Ab} = 12.0 \left(1 - X_{Pl}^2 Ab\right)^2 - 3.0 \text{ kJ}$, $R = 0.0083144 \text{ kJ} \text{ K}^{-1} \text{mol}^{-1}$, and various cation $X$ terms are summarized in Appendix 1. The average mole fraction of albite in
plagioclase ($X_{Ab}^m$) 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 [10, 14].

The above equation yields low temperatures ($\leq 700 \, ^oC$), ranging from 617 to 700 $^oC$ (Table 1). The lower part of the range is build up by samples from granodiorite. The temperatures from granite are wider in range and higher in values, compared with granodiorite. This may be related to substantial decrease in the contents of biotite and amphibole in granite. In fact, decrease in hydrous silicates means low $H_2O$–content of melt, drier condition and elevating temperature [15]. The calculated temperatures represent a mean value of 650 $^oC$ which is in the vicinity of $H_2O$–saturated granite solidus at low pressures (2–2.5 kbar) and is consistent with quartzofeldspathic nature of the studied rocks. The range of calculated temperatures is similar to water–rich felsic I–type magnetite–granites from Australia [e.g. 15] which formed in low temperatures (620–722 ± 7 $^oC$).

Comparison of the $T_A$ (617–700 $^oC$) data from this study with $T$ data for mafic low–temperature I–type granites (700–800 $^oC$) of the Lachlan Fold Belt (LFB), Australia [16a,b] shows a lower temperature for felsic rocks of the Kashmar granitoid. This comparison results in a thermal boundary of ≈700 $^oC$ to be proposed as a calculation scheme for distinction between mafic and felsic low–temperature I–type granites. Hence, the modern subdivision of I-type granites is reinforced to further development.

**Pressure Revised**

To obtain a revised estimate of pressure of crystallization for amphibole from plutonic rocks, using experimental data at ~675 $^oC$ [9] and at ~760 $^oC$ [6], Anderson and Smith [8] generated the temperature–dependent barometer (of equation 3):

$$P_{AS} (\pm 0.6 \text{kbar}) = 4.76 Al^T - 3.01 - \{1(T - 675)/85\} \times \{0.530 Al^T + 0.005294[T - 675]\}$$

where, $T$ is the Celsius temperature calculated from equation 2 and $Al^T$ is the total number of $Al$–cations in the hornblende calculated via 13eCNK.

Using the above barometer, the revised estimated pressures ($P_{AS}$) are very similar to calculated $P_S$ values (Table 1) specified by equation 1. For any given sample, $P_{AS}$ is less or more by a little amount ($\leq 0.2 \text{kbar}$) than $P_S$, indicating the reliability of the calculated $P$ data (Fig. 1D). 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 (always
X_{Ab}^{pi} > 0.50 \text{ moles } \rightarrow Y_{Ab} = 0); \text{ 4) the Mg and Fe contents of these amphiboles are within the limits established by [8, 9, 14] for P–T determination using thermo–barometer of [13].}

**Oxygen Fugacity (fO₂)**

To clarify the fO₂ stability of the Kashmar granitoid, the equilibrium expression of Wones [12] is used as the following (equation 4):

$$\log fO_2 = -30930/T_A + 14.98 + 0.142(P_S - 1)/T_A \text{ (eq.4)}$$

where, $T_A$ is temperature (in Kelvin’s) and $P_S$ is pressure (in bars) calculated by equations 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 [12], the conditions are adopted for the present study. Using the equation 4, logfO₂ was calculated for Kashmar amphiboles and listed in Table 1. The calculated values of logfO₂ shows a restricted range from –19.40 to –16.59 with an average –18.31, confirming all petrological and mineralogical context that inferred oxidation conditions for the Kashmar granitoid. The obtained values of logfO₂ are moderately low because of the slight incorporation of pressure, low values of $P_S$ and $T_A$ which are substituted in Wones’ equation [12]. 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 °C), oxidized (logfO₂ = –15) I–type granites of the LFB [15]. A plot of 10,000/T(°k) vs. logfO₂ provides linear trend (Fig. 1E) well above the stability of FMQ ($Fe_2SiO_4 + Fe_3O_4 + SiO_2$), between the NNO ($Ni + NiO$) and HM ($Fe_2O_3 + Fe_3O_4$) buffers, a feature attributed to oxidized, I–type granites [16a,b] and consistent with emplacement of Kashmar granitoid in an iron–oxide reservoir type belt [18].

Typical ilmenite–granites contain hornblende with Fe/(Fe + Mg) ratios of 0.80 to 0.99 [8] but hornblendes from this study are low in Fe/(Fe + Mg) ratios (≤ 0.50), suggesting early magnetite crystallization and oxidized condition. The calculated $T$ and logfO₂ values for Kashmar amphiboles are essentially different from typical dry, S–type, ilmenite–granites of the LFB. Major differences include: higher temperature (>800 °C), wider range of T (860–1026±7 °C) and lower fO₂ (below FMQ) for S–type granites [15]. These differences are reflected from the source composition, but the availability of H₂O in I–type granites largely determines $T$ and fO₂ conditions. In the present work, the range of $T$ and $P$ are similar to H₂O–saturated magmas of tonalite to granodiorite composition [14] 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 Kashmar granitoid. The composition of Kashmar amphiboles was appropriate for utilization of principal thermo–barometers, yielding the satisfactory results of $T$ (617–700 °C), $P$ ($\leq 3$ kbar) and log $f_{O_2}$ ($-16.59$ to $-19.40$) 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 °C). This lower temperature range is consistent with the quartzofeldspathic nature of the Kashmar granitoid (ASI = ~1) and 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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Appendix 1 Calculation of mole fractions and assignment of site occupancies for Ca–amphiboles from the Kashmar granitoid, NE Central Iran Plate.

### Amphibole

- **$T_1Si$** = $Si - 4.0$
- **$T_1Al$** = $8.0 - Si$
- **$M^2Ti$** = $Ti$
- **$M^2Al$** = $Al + Si - 8.0$
- **$M^2Fe^{3+}$** = $Fe^{3+}$ (if any)
- **$M^2Fe$** = $[2 - (M^2Al + M^2Ti + M^2Fe^{3+})] \times Fe/(Fe+Mg)$
- **$M^2Mg$** = $[2 - (M^2Al + M^2Ti + M^2Fe^{3+})] \times Mg/(Fe + Mg)$
- **$\delta Na$** = $(Si + Al + Ti + Fe^{3+} + Mg + Fe + Mn + Ca + Na) - 15$
- $\delta_A$ = $1 - \delta Na - K$
- $X_{T1Si} = T1Si/4.0$
- $X_{T1Al} = T1Al/4.0$
- $X_{M2Al} = M2Al/2.0$
- $X_{M2Mg} = M2Mg/2.0$
- $X_{M2Fe} = M2Fe/2.0$
- $X_{\delta Na} = \delta Na$
- $X_{\delta A} = A$

$\square$ refers to the alkali site vacancy.

### Plagioclase

- **$X_{PlAb}$** = $Na/(Ca + Na + K)$

In this study, the average mole fraction of albite in plagioclase ($X_{PlAb}$) is always $>0.50$ → $Y_{Ab} = 0$

Note: 1) 13eCNK means the normalizing of the cations to the $(13/\sum \text{cations} - \text{Ca-Na-K})$ value on the presumption that $Fe^{2+}$, Mg, and Mn do not occupy $[M4]$; 2) The ratios $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ and $Fe_{tot}/(Fe_{tot} + Mg)$ 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 and any data which are not acknowledged in the text, are from author’s Ph.D. thesis [1].