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ترکیب شیمیایی آمفیبول در گرانیتهای نوعI با دمای پایین از منطقه کاشمر شمال شرقی ایران مرکزی

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چکیده: گرانیتوئید کاشمر (4 - 47/4 - 47/4) بخش وسیعی از کمربند ماگمایی تیپ اکسید آهن را در شمال گسل درونه تشکیل می دهد. تودههای نفوذی آن شامل تونالیت، گرانودیوریت، گرانیت و آلکالی فلدسپار گرانیت است که همگی از لحاظ درجه اشباع آلومینیم، متالومین ($4 \le 1 \le 1$) اند. کانیهای آنها عمدتاً فلسیک و خواص گرانیتهای نوع -1 با دما و فشار پایین را نشان می دهند. طبق مطالعات میکروسکوپی و آنالیزهای الکترون مایکروپروب، آمفیبولهای کاشمر همگی از نوع مونوکلینیک کلسیک هورنبلند هستند. این کانی، شاخص عمده در شناخت گرانیتهای نوع -1 می باشد. فرمول ساختمانی آن با رعایت کامل استاندارد محاسبه شده و خواص برجسته زیر را نشان می دهد:

واژههای کلیدی: کلسیک آمفیبول، مگنزیوهورنبلند، گرانیتوئید، کاشمر، نـوع I^- دمـای پـایین، ایران مرکزی.





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Amphibole Chemistry in Low-temperature I-type Granites from Kashmar Area, Northeastern Central Iran Plate (CIP)

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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 \leq 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:

Ca(M4)+Na(M4)>1.34, Na(M4)<0.67, Mg*>0.50, (Na+K)A<0.50, Ti<0.50 apfu. They are low in Al $_2$ O $_3$ and TiO $_2$, high in Mg* (0.6–0.75), extremely low in Al $_2$ I (<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 \leq 3 kb and logfO $_2$ = -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 wholerock geochemistry of Lachlan Fold Belt (LFB) I-type granites. The wholerock emphasizes the concentration of REE, Zr, P, Ba, Rb and their pattern of variation in Harker plots. However, in some cases high- and lowtemperature 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 lowtemperatures; 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 andesitic 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 ± ilmente. 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 Itype 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 (Fe³⁺) 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 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 than 0.5 atoms per formula unit (apfu), representing typical magnesio—hornblende with formulae of $Ca_2[Mg_4(Al,Fe^{3+})][(Si_7A)O_{22}](OH)_2$ which is distinct mafic mineral in I—type granites. The studied hornblendes are chemically homogeneous in composition and high in $Mg^* = Mg/(Mg+Fe^{2+})$ ratios which range from 0.60 to 0.75. Their total Si varies from 6.800 to 7.155 apfu, features confirming magnesio—hornblende.

The analyzed hornblendes are characteristically low in Al_2O_3 (4.67 to 7.17 wt%, $Al^T < 1.3$ apfu), Na_2O (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 ($Fe^{3+} > Al^{VI}$) suggest no Tschermaks and edenite substitutions, respectively [3, 4]. Octahedral Al (Al^{VI}) is less than 0.1 apfu and Fe^{3+} is about ten times higher than Al^{VI} , 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 fO₂ 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-fO₂ conditions [5, 7]. Because at higher fO₂, 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 $0.4 \le Fe^{tot}/(Fe^{tot} + Mg) < 0.65$, 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:

$$P_{\rm S}$$
 (±0.6) = 3.01 + 4.76 Al^T, r2 = 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 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 (\leq 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 AI^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 AI^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).

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_2O_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
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
AlIV	1.076	1.200	0.936	0.853	1.067	1.157	1.000	0.803
AlVI	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⁺ /Fetotal	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}^{Pl} (mole)	0.65	0.65	0.64	0.64	0.66	0.66	0.62	0.62
Ps (kbar)	2.32	2.97	1.49	1.13	2.41	2.95	1.75	0.81
PAS (kbar)	2.51	3.21	1.31	1.25	2.60	2.91	1.72	0.91
TA (°C)	617	621	700	627	633	680	680	642
$\log f O_2$	-19.40	-19.15	-16.59	-19.21	-19.16	-17.04	-17.22	-18.69

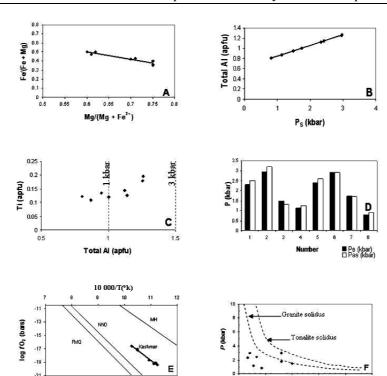


Figure 1 Compositional variation and $P-T-fO_2$ conditions for Kashmar amphiboles. (A) Contrary trend between Mg* and Fe/(Fe + Mg) ratios. (B) Positive correlation between calculated Ps and total Al–content of hornblende. (C) Total Al versus Ti contents with pressure contours determined according to [6]. (D) Similarity between calculated Ps (independent of temperature) and the revised estimated pressures (P_{AS}). (E) Plot of log/O_2 (bars) versus $10000/T(^{\circ}K)$ showing oxidation state well above the FMQ, between MH and NNO buffers, with phase boundaries after Wones [12]. (F) Diagram showing P(kb) versus $T(^{\circ}C)$ for Kashmar amphiboles which occur in the vicinity of solidus. The solidus lines are after [17].

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 hbld–plag thermometer of [13] which is shown as equation 2:

$$T_{A}\left(\pm 40 \,^{\circ}C\right) = \frac{-76.95 + 0.79P + Y_{Ab} + 39.4X_{Na}{}^{A} + 22.4X_{K}^{A} + \left(41.5 - 2.89P\right)X_{Al}^{M2}}{-0.0650 - R^{\bullet}ln\left[\left(27X_{\square}^{A}, \bullet X_{\square}^{T1}S_{I} \bullet X_{\square}^{P1}A_{b}\right)/\left(256X_{Na}^{A} \bullet X_{\square}^{T}A_{l}\right)\right]} - 273\left(eq.2\right)$$

where, T_A is amphibole temperature (°C), P is pressure (kbar) calculated from equation No. 1, $X_{Ab}^{Pl} > 0.5$: $Y_{Ab} = 0.0$ or else $Y_{Ab} = 12.0 (1-X_{Ab}^{Pl})^2 - 3.0$ kJ, R = 0.0083144 kJK⁻¹mol⁻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 [10, 14].

The above equation yields low temperatures (≤ 700 °C), ranging from 617 to 700 °C (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 H₂O-content of melt, drier condition and elevating temperature [15]. The calculated temperatures represent a mean value of 650 °C which is in the vicinity of H₂O-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 °C).

Comparison of the T_A (617–700 °C) data from this study with T data for mafic low–temperature I–type granites (700–800 °C) 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 \approx 700 °C 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 °C [9] and at ~760 °C [6], Anderson and Smith [8] generated the temperature–dependent barometer of (equation 3):

 $P_{\rm AS}$ (±0.6 kbar)=4.76Al^T - 3.01-{[T - 675]/85}×{0.530Al^T + 0.005294[T - 675]}(eq 3) 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 (≤ 0.2 kbar) than P_S , indicating the reliability of the calculated P-T 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

 $X_{Ab}^{Pl} > 0.50$ moles $\rightarrow Y_{Ab} = 0$; 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):

$$\log f O_2 = -30930/T_A + 14.98 + 0.142(P_S - 1)/T_{(A)}$$
 (eq. 4)

where, T_A is temperature (in Kelvin's) and P_S is pressure (in bars) calculated by 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 show 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 $P_{\rm S}$ and $T_{\rm A}$ 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 ($\log fO_2 = -15$) I-type granites of the LFB [15]. A plot of 10,000/T(°k) vs. log/O₂ provides linear trend (Fig. 1E) well above the stability of FMQ (Fe₂SiO₄ + Fe₃O₄ + SiO₂), between the NNO (Ni + NiO) and HM (Fe₂O₃ + Fe₃O₄) 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 H_2O 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 $\log fO_2$ (–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 = \sim 1) and recommends a thermal boundary of \sim 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 \sim 700 to 800 °C for mafic compositions, and \sim 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.

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Amphibole
    ^{T1}Si= Si - 4.0

\begin{array}{lll}
^{11}SI = SI - 4.0 \\
^{11}AI &= 8.0 - Si \\
^{11}M^{2}Ti &= Ti \\
^{11}M^{2}AI &= AI + Si - 8.0 \\
^{11}M^{2}Fe^{3+} &= Fe^{3+} (if any) \\
^{11}M^{2}Fe &= [2 - (^{M2}AI + ^{M2}Ti + ^{M2}Fe^{3+})] \times Fe/(Fe + Mg) \\
^{11}M^{2}Fe &= [2 - (^{M2}AI + ^{M2}Ti + ^{M2}Fe^{3+})] \times Mg/(Fe + Mg)
\end{array}

   ^{M2}Mg = [2 - (^{M2}Al + ^{M2}Ti + ^{M2}Fe^{3+})] \times Mg/(Fe + Mg)
    ^{A}Na = (Si + Al + Ti + Fe^{3+} Mg + Fe + Mn + Ca + Na) - 15
   A_{\square} = 1 - {}^{A}Na - K
                  = 16 - (Si + Al + Ti + Fe^{3+} + Mg + Fe + Mn + Ca + Na + K)
   X^{T1}_{Si} = {}^{T1}Si/4.0

X^{T1}_{Al} = {}^{T1}Al/4.0
\begin{array}{lll} ... & _{Si} & - \cdot \cdot SI/4.0 \\ X^{T1}{}_{AI} & = ^{T1}AI/4.0 \\ X^{M2}{}_{AI} & = ^{M2}AI/2.0 \\ X^{M2}{}_{Mg} & = ^{M2}Mg/2.0 \\ X^{M2}{}_{Fe} & = ^{M2}Fe/2.0 \\ X^{A}{}_{A}. & - ^{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A}{}_{A
   X^{A}_{Na} = {}^{A}Na
   X_{\square}^{A} = A_{\square}
   \Box = refers to the alkali site vacancy.
   Plagioclase
   X^{Pl}_{Ab} = Na/(Ca + Na + K)
   In this study, the average mole fraction of albite in plagioclase (X_{Ab}^{Pl}) is always >0.50\rightarrow Y_{Ab} = 0
   Note: 1) 13eCNK means the normalizing of the cations to the (13/\Sigma^{\text{cations}}) –Ca–Na–
   K) value on the presumption that Fe<sup>2+</sup>, 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
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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].