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CO_2-H_2O, Highly Saline and Carbonic Fluids from the Mesozoic Mashhad Granitoids, NE Iran

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Abstract

The Mesozoic Mashhad granitoid plutons have intruded into ophiolite complexes, meta-sediments and pyroclastics in the Binalood region, located SW of Mashad city in the NE part of Iran. Based on petrography and geochemistry, the Mashhad granitoids have been classified into 1) grey granite, 2) pink granite, 3) muscovite granite, 4) granodiorite and 5) pegmatite and quartz veins. Granitoids show typical igneous micro-textures with the mineral assemblage of quartz, plagioclase, K-feldspar, biotite, muscovie, amphiboles, clinopyroxene and garnet. Based on two-feldspar thermometry and hornblende-plagioclase thermometry / barometry, igneous temperatures of 750 to 770°C and pressures of 4.6 to 5.5 kbars for the emplacement of granitoids have been estimated. The granitoids of Mashhad area have been classified as moderately peraluminous, S to I type granitoids of sub-alkaline to calcic type.
Fluid inclusion study on Mashhad granitoids shows the presence of Isolated Fluid Inclusions (IFI) as well as Trail Bound Inclusions (TBI). Four types of fluid inclusions viz., Type I CO_2-H_2O inclusions, Type II Low salinity aqueous inclusions, Type III, high salinity inclusions and Type IV Carbonic inclusions have been recorded in Mashhad granitoids. Fluid inclusions occur as rounded, oval and negative crystal shape varying in size from 5 to 16 μm. CO_2-H_2O fluids are the most common fluids in Mashhad granitoids. CO_2 in CO_2-H_2O inclusions varies from 20 to 80 percent. Minor bi-phase, low salinity aqueous inclusions occur. Presence of Type III, Halite bearing fluids are found mainly in quartz veins in granodiorite. Type IV, carbonic fluids occur along late fractures which cross-cut the early Type I, CO_2-H_2O fluids.
CO_2 in CO_2-H_2O inclusions shows Tm around -56.8 °C, indicating almost pure carbonic inclusions. TmClath vary from 4 to 8°C. Th of CO_2 in liquid phase ranges from - 9 to 22° C with densities of 0.92 to 0.68 g/cc and the total homogenization of CO_2-H_2O ranges from 205 to 320°C, indicating XCO_2 valuesof 0.75 to 0.20 mole fraction. The bi-phase fluid inclusions show low salinity values of 4 to 8 wt. % NaCl equivalent to 1.03 to 0.96 g/cc. Type-IV, late carbonic inclusions show Th ranging from 20 to 25°C with densities from 0.82 to 0.78 g/cc. Tye III, halite bearing fluids show temperatures of melting from 315 to 335°C with salinity values of 38 to 40 wt. % NaCl equivalent.
The density data of fluids in Mashhad granitoids indicates entrapment temperatures of 590 to 650°C at pressures of 4.1 to 5.2 Kbar. This data nearly coincides with the mineral P-T estimates. There are strong evidences of "fluid-present" partial melting process during the formation of S-type and I-type granitoids in Mashhad area. The low density carbonic fluids are chronologicaly late fluids trapped in granitoids, formed due to the peferential leakage of water from the early CO_2-H_2O inclusions. Fluid leakage is related to ductile shear deformation along thrust zones in Mashhad granitoids.

***Key words**: Fluids, Mashhad granitoids.*

1. Introduction

Presence of different types of fluids like H_2O, H_2O-NaCl, CO_2 and CO_2-H_2O and CH_4 has been reported in many granitic rocks. Fluid inclusion study in granites are important as they provide necessary information on the nature and composition of fluid phase associated with felsic magmas. Experimental work on granitic rocks has shown the significant role of volatiles in the generation, mobility and crystallization of granitic melts. H_2O fluids were thought to be the most dominant fluid phase in felsic melts.

However, the recent fluid inclusion studies in many deep-seated granitic intrusions, particularly from the Precambrian terranes have shown the presence of not only H_2O bearing fluids but also presence of CO_2, mixed CO_2-H_2O and halite bearing fluids in granitic rocks [1, 2, 3]. The origin of S- and -type granitic rocks has been discussed in detail [4]. The S-type granites have been formed by partial melting of crust dominated by metasediments with few igneous rocks and I-type granites have been formed due to partial melting of crust dominated by meta-igneous rocks with minor meta-sediments. The process of partial melting leading to formation of granites could be either by fluid-present or fluid-absent process [4,5]. Fluid inclusion studies in granites is significant not only to characterise the

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nature and composition of fluids associated with granitic magmas but also to understand the “fluid-absent” or “fluid present” process during the formation and accent of granitic magma.

Data on the type of fluids present in Mesozoic granitoids from Mashhad (Iran) is not available, although geology of the area around Mashhad has been well documented [6,7,8,9,10]. Petrographic and a few mineral chemical data have been reported on the Mashhad granite [8,9]. Except for the preliminary report of low salinity and CO_2-H_2O fluids in a quartz vein, intruding Mashhad granitoids [11], information on the nature and composition of fluids associated with Mashhad granitoids is completely lacking. In this paper, we report for the first time presence of four different types of fluids like CO_2-H_2O, low saline, highly saline and carbonic fluids in Mashhad granitoids.

2. Geology of the area

The Mesozoic Mashad granitoid plutons (MMGP) are situated in the Binalood region located SW of Mashad city in NE part of Iran [6,7]. The paleo-tethys remnants consist of three assemblage of rocks viz., (1) ophiolites consisting of peridotites, pyroxenite, isotropic gabbros, and basalts; metacherts are interbedded with thinly bedded marbles which are interlayered with metabasalts, (2) metamorphosed sedimentary sequence consisting of slates, phyllites, schists, carbonates and metaconglomerates and (3) pyroclastics – a distinctive assemblage of interlayered metamorphosed lapilli-tuffs and tuffs in the Binalood region form a long and narrow belt which extends for several kilometers in a NW-SE direction [7]. The granitoids have intruded the ophiolite complexes and meta-flysch during the Mesozoic period [7,8]. There are two main varieties of granitoids viz., 1) S-type, continental collision / syn-collisionnal muscovite granite and pegmatite and 2) I-type, within the plate, post-collisional hornblende and green biotite bearing granite. Based on the isotopic ages, mineral composition and bulk rock composition [8,9] there are three varieties of granitoids viz., 1) biotite granodiorite and biotite quartz monzodiorite which represent the oldest intrusives, 2) feldspar-granite and 3) biotite- muscovite granite and aplite granite which represent the final stage of magmatic activity. On the basis of petrographic study [9] the granitoids have been classified into five major groups viz., 1) biotite granite 2) muscovite granite 3) hornblende granite 4) pegmatite 5) aplite. Three episodes of magmatism have been identified in the Mesozoic Mashhad granitoid pluton (MMGP). The first episode of magmatism is recorded near Dehnow, where there is evidence for hornblende-biotite bearing tonalite and granodiorite having intruded after the first regional metamorphism before the late Triassic to early Jurassic period. These rocks were classified as moderately peraluminous, S- to I- type granitoids of sub-alkaline to calcic type. It has also been suggested that biotite bearing granodiorite exposed around Vakilabad and Kuhsangi area belongs to the oldest member of the granitoid suite. During the second phase of igenous activity which occurred during the late Triassic period, feldspar monzogranite exposed near Sangbast area were intruded. Field and structural relations show that these intrusives are younger than the granodiorite and older tan the biotite-muscovite leucogranite. They are moderately peraluminous, K-rich calc-alkaline type. The last stage of magmatism took place during Jurassic time. This indicates an episodic plutonism from the early Triasic to Cretaceous period. Four main types of enclaves have been identified in biotite-muscovite leucogranite viz. feldspar- monzogranite, metamorphic rocks, biotite-granodiorite and micaceous rich grey intrusive in this granitoid pluton. The Khajehmourad, biotite-muscovite leucogranite and late pegmatite dykes are highly felsic peraluminous S-type granitoids in the area [8,9]. A major NW-SE trending thrust fault (shear zone), demarcates the western margin of the Mashhad graniotoids (Fig.1). Granitoids are relatively undeformed with the exception of ductile shears cutting the granitoids near Dehnow. Near Dehnow, N-W to SE trending ductile shears with the development of mylonitic to ultramylonitic fabric are observed. These features suggest considerable reactivation along a NW-SE trending thrust zone, along the western margin of the granitoids near Dehnow. For the purpose of fluid inclusion study, the Mashhad granitoids have been classified into 1) grey granite 2) pink granite 3) muscovite granite 4)granodiorite and 5) pegmatite and quartz veins based on the petrography. Granitoids show typical igneous micro-textures with the mineral assemblage of quartz, plagioclase, K-feldspar, biotite, muscovie, amphiboles, clinopyroxene and garnet. Quartz shows straight to lobate grain boundaries. Quartz grains show flash figures and do not exhibit undulose extinction. These features indicate that quartz grains are largely undeformed. A few quartz grains show the presence of intragranular fractures. Euhedral plagioclase grains are generally fresh. They often contain euhedral grains of muscovite. In some granites, plagioclase shows alteration to sericite and talc mainly in the central portions with margins of these grains being free from any alteration. Flaky biotite occurs between quartz and plagiolcae grains and is pleochroic from brown to yellow -brown. Undeformed microcline occurs as tabular grains exhibiting typcial cross-hatched twinning. Within the bigger microcline grains, presence of smaller, euhedral grains of twinned plagioclase is commonly observed. Based on two-feldspar thermometry and hornblende-plagioclase thermometry / barometry, igneous temperatures of 750 to 770^{o}C and pressures of 4.6 to 5.5 kbars for the emplacement of granitoids have been estimated.

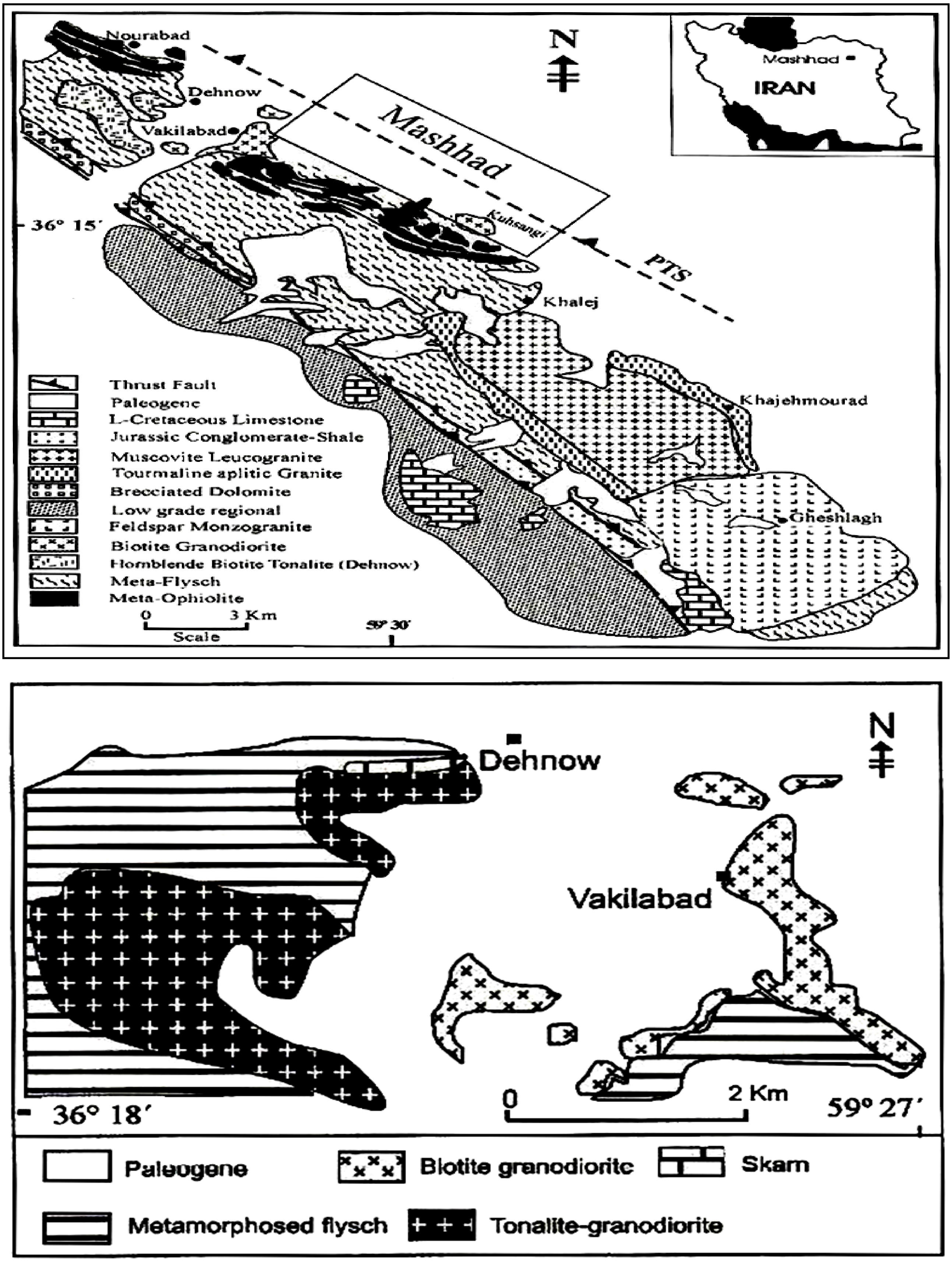

Fig. 1. Geological map of the study area-Mashhad, NE-IRAN (after Karimpour, M, H, 2006)

3. Fluid Inclusions Petrography

Methods of Fluid Inclusion study:
Microthermometric measurements on fluid inclusions were obtained on a LINKAM -THMS 600 and CHAIXMECA apparatus mounted on a LEITZ LABORLUX-12 microscope with a 40X objective at university of Mysore, Mysore. Cooling experiments were carried out before heating of doubly polished sections to avoid the possibility of loss of inclusions during heating due to decrepitation. The stage was calibrated using different standards and the precision was ± 0.1°C at low temperatures and ± 1.0 °C at high temperatures.

Fluid inclusion petrography: Fluid inclusions studies were carried out for 15 rock samples. However, in only five rock samples good number of fluid inclusions have been recorded in the matrix quartz grains. Very small fluid inclusions were noticed in plagioclase feldspar and fluids were absent in microcline.
Fluid inclusions were classified based on the orientation of fluid inclusions within the mineral into primary and pseudosecondary inclusions following Roedder (l2). Fluid inclusions were classified into Isolated Fluid Inclusions (IFI), which are primary inclusions in minerals and Trail Bound Inclusions (TBI), which are intragranular, fracture - bound secondary inclusions in minerals. Based on the distribution pattern of inclusions, the isolated inclusions are classified as Group of Synchronous Inclusions (GSI) [13]. In this paper, we use the term GSI to describe the trail bound inclusions in quartz grains. Care has been taken to record the textural relationship between fluid inclusions and the host mineral to document the relative timing of fluid entrapment which is a prerequisite for meaningful interpretation of fluid inclusion data [14].

Chronology of fluids inclusions: Based on microtextural features of the matrix quartz grains and the shape, size and orientation of different types of fluids recorded in Mashhad granites, the relative timing of entrapment of fluid inclusions has been established. The chronology of fluids is discussed in the following section.

Fluid inclusion study: Fluid inclusion study was carried out on five rock types viz., grey granite, pink granite, muscovite granite, granodiorite and pegmatites exposed around Mashhad. The following three types of fluid inclusions have been recorded:

Type I CO_2-H_2O inclusions
Type II Low salinity aqueous inclusions
Type III High salinity inclusions and
Type IV Carbonic inclusions

Fluid inclusions occur as rounded, oval and negative crystal shape. They are either irregularly distributed within the quartz grains or occur as intragranular trail bound inclusions. They vary in size from 5 to 16 μm. CO_2-H_2O fluids are the most common fluids recorded in quartz grains in Mashhad granitoids (Fig. 2). They appear bi-phase at room temperature. The volume proportion of CO_2 in CO_2-H_2O inclusions varies from 20 to 80 percent, suggesting a highly varying mole fraction of CO_2 in inclusions. Minor, bi-phase, low- salinity aqueous inclusions occur coeval with CO_2-H_2O inclusions. Fluid inclusion petrography and chronology of fluid entrapment data indicate the presence of Type I, CO_2-H_2O which are the most common fluids which occur with low salinity aqueous systems.
These Type I and Type II fluids represent the earliest fluids trapped in Mashhad granitoids. Type II, halite - bearing, highly saline fluids are found mainly in a quartz vein which cross cuts the granodiorite. Halite bearing inclusions are randomly distributed within the quartz grains with sizes varying from 14 to 18 μm. These inclusions are classified as GSI.
Type IV, carbonic fluids occur along late fractures which cross-cut the early Type I, CO_2-H_2O fluids (Fig.3). These CO_2-rich fluids appear as dark inclusions, show negative crystal shapes to highly irregular shapes. Their sizes vary from 10 to 15 μm. These inclusions are the only inclusions which occur along an intragranular trail within the quartz grains and are classified as TBI.

Microthermometric results: CO_2 in CO_2-H_2O inclusions shows melting temperatures (Tm, CO_2) around -56.8 ^oC, indicating nearly pure carbonic inclusions (Table 1). TmClath varies from 4 to 8^oC. Temperature of homogenization of CO_2 into liquid phase range from - 9 to 22^o C, indicating a density of 0.92 to 0.68 g/cc.

The total homogenization of CO_2-H_2O inclusions ranges from 205 to 320^oC, indicating X_{CO2} values varying from 0.75 to 0.20 mole fraction [19]. The bi-phase fluid inclusions show Tm from - 5 to - 2^o C with low salinity values from 4 to 8 wt % NaCl equivalent. They show homogenization into liquid phase varying from 120 to 160°C, indicating a density of 1.03 to 0.96 g/cc. Type-IV, late carbonic inclusions show Th ranging from 20 to 25°C with density of 0.82 to 0.78 g/cc. A few halite- bearing type III fluids in quartz vein cross cutting the granodiorite show temperatures of halite melting at 315 to 335^oC, indicating high salinity values of 38 to 40 wt.% NaCl equivalent.

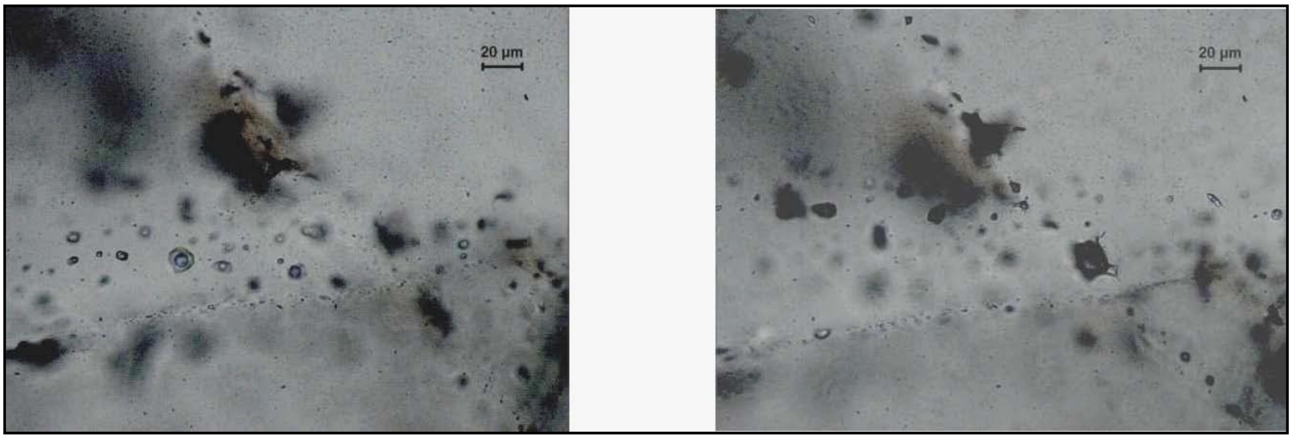

Fig. 2. (Left)Bi-phase CO_2-H_2O inclusions in quartz from Granite

Fig. 3. (Right) CO_2-rich inclusions aloong late fracture cross cutting CO_2 –H_2O inclusions in quartz.

Fig. 2 & 3. Fluid inclusions in quartz-granitoids of Mashhad Table 1 Microthermometric result of fluid inclusions from Granitoids of Mashhad, NE-IRAN

Table 1. Microthermometric results of fluid inclusions from Granitoids of Mashhad, NE-IRAN

Rock Type		**CO_2 – H_2O inclusions**			**CO_2 inclusions**			**H_2O -NaCl inclusions**		
		T_m CO_2 GSI	Th CO_2	Th_{total}	T_m	T_h (TBI)	d	Tm	Tm Wt % NaCl equiv.	dg/cc
M-6/1	Granodiorite	–57.8	–10 to –14							
M-6/3	Pink Granite	– 57.8	-4 to -2	255 to 290	–57.9	20 to 25	0.82 to 0.78	–2 to –5	4 to 8 120 to 160	1.03 to 1.96
M-4/1	Muscovite-Granite	–57.8 to –57.5	– 9 to –2	190 to 275						
M-5/2	Tourmaline-Pegmatite	–57.9	10 to 16	290 to 320						
M-7/2	Grt – bearing Pegmatite	– 57.8	10 to 21	260 to 295						
M - 11/4	Quartz vein	–57.9	10 to 22	170 to 245	Tm of Halite varies from 205 to 220°C					

Abbreviations used in the table:

GSI: Group of synchronous fluid inclusions TBFI: Trial bound fluid inclusions Tm: Temperature of melting
Th: Temperature of homogenization (Tm &Th are represented in degrees centigrade; °C)
Th (tot): Total homogenization of CO2-H2O; d: density represented in g/cc. CLA: Clathrate melting.
M-6/1: Granodiorite, Qtz+Kfs (perthite) +Pl+Bt+Am. GPS – 36° 5' 12.1" E 59° 38'47.4"
M-6/3: Pink Granite, Qtz+Kfs (perthite) +Pl+Bt+Ms+Opq+Ser. GPS – 36° 5' 12.1" E 59° 38'47.4"
M-4/1: Muscovite Granite Qtz+Kfs (perthite) +Pl+Bt+Ms. GPS– N 360 09° 1'17.5" E 59° 37' 50.2"
M-5/2: Tourmaline Pegmatite, Qtz+Pl+Ms+Tur, GPS – N 36° 06' 27.7" E 59° 38' 43.9"
M-7/2: Garnet –bearing Pegmatite, Qtz+Pl+Kfs+Ms +Grt. GPS – N 36° 08' 59.8" E 059° 42' 21.9"
M-11/4: Quartz vein, Dehnow. GPS – N 36° 21' 43.9" E 59° 24' 42.1"

4. Conclusions

- Mashhad granitoids and pegmatites are largely undefomed igneous bodies which have intruded into the meta-ophiolites and metamorphosed flysch during the Mesozoic period. Mashhad granitoids are undeformed igneous bodies and show typical igneous micro-textures. Quartz in all the rock types studied show no signs of deformation and is considered to represent igneous mineral. However, quartz in mylonites and ultramylonites shows the process of recovery and recrystallization features with the development of quartz neo-blasts.

- The most common type of fluids recorded in all the granitoids as well as in pegmatite and quartz veins is the CO_2-H_2O type. These fluids occur co-eval with low salinity aqueous fluids within quartz grains. The CO_2-H_2O inclusions show varing volume proportions of CO_2 indicating mole fraction of CO_2 varying from 0.75 to 0.20. In quartz veins, cross-cutting the granodoirite, presence of primary halite bearing fluids has been recorded with high salinity values of 38 to 40 wt.% NaCl equivalent. Based on the intersection of density data of these fluids, entrapment temperatures ranging from 590° to 650°C at pressures of 4.1 to 5.2 kbar are estimated. Slighly lower pressure and temperature estimates were obtained based on fluid inclusions study when compared to P-T data obtained based on two-feldspar and hornblende-plagioclase thermometers . These could be due to moderate reequilibration of fluids probably during uplift of the granitoids. Based on these observations, the primary CO_2-H_2O, low salinity aqueous fluids as well as high salinity halite- bearing fluids are interpreted to represent magmatic fluids trapped in Mashhad granitoids. All these evidences indicate fluid-present partial melting process during the formation of S-type granites in Mashhad area. The presence of predominantly CO_2-H_2O fluids in granodiorites as well as both CO_2-H_2O and highly saline fluids in late quartz veins suggest fluid evolution with the enrichment of saline fluids during late magmatic stage in Mashhad granitoids. The present fluid inclusion study brings to light the significance of CO_2-H_2O and highly saline fluids in understanding the petrogenesis of granitic rocks, and particularly the origin and evolution of S-type granitoids [6].

- Presence of low denstiy (0.78 to 0.82 g/cc) carbonic fluids along intragranular fractures in quartz grains indicates that these are the chronologicaly later fluids trapped in granitoids. The carbonic fluids have formed due to the peferential leakage of water from the early CO_2-H_2O inclusions along micro-fractures. This process is related to ductile shear deformation along thrust zones, which led to formation of carbonic fluids in Mashhad granitoids.

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References

[1] Konnerup-Madson, J., (1979), Fluid inclusions in quartz from deep- seated granitic intrusion, southern Norway, Lithos, v. 12, p.13-.23

[2] Frezzotti, M.L., Di Vincenzo, G., Ghezzo, C., Burke, E.A.J, 1994, Evidence of magmatic CO2- rich fluids in peraluminous graphite-bearing leucogranites from Deep Freeze Range Contrib. Mineral. Petrol., v.117, p.111-123.

[3] Nabelek and Ternesm., 1994, Evidence of magmatic CO2-rich fluids in peraluminous graphite -bearing leucogranites from Deep Freeze Range. Contrib. Mineral.Petrol., v.117, p.111-123.

[4] Clemens, J.D., 2003, S-type granitic magmas - petrogenetic issues, models and evidences. Earth. Science Reviews, v. 61, p. 1-18.

[5] Clemens, J.D., and Droop, G.T.R., 1998, Fluids, P-T paths and fates of anatectic melts in the Earth’s crust. Lithos, v. 44, p. 21-36.

[6] Alavi, M., Thrust tectonics of the binaloud región; NE Iran. Tectonics, v. 11(2), p.360-370.

[7] Alavi, M., 1991, Sedimentary and structural characteristics of the Paleo-Tethys remnants in Northeastern Iran. Geophysical Unión, Geol. Soc. America Bull., v.103, p. 983-992.

[8] Karimpour, M.H., Farmer, L., Ashouri, C., and Saadat, S., 2006, Major,Trace and REE Geochemistry of the collision-Related Granitoids from Mashhad, Iran. Jour. Sciences, Islamic Republic of Iran, v. 17(12), p.127-145.

[9] Karimpour, M.H., Farmer, L., Ashouri, C.and Saadat, S., 2002, Petrogenesis, paleotectonic setting, metallogeny of Mashhad paleo-tetys granitoids, Iran, Denever anual meeting Colorado convention centre.

[10] Iranmanesh, J. and Sethna, S.F., 1998, Petrography and geochemistry of the Mesozoic Granite at Mashhad, Khorasan Province, Northestern part of Iran. Jour. Geol. Soc. India, v.52, p. 87-94.

[11] Tecca, F., Masoudi, F., Shabani, A.A.T., and Tarokh, A, 2009, CO2-bearing fluids in quartz Veins intruding the Mashhad granitoids, NE Iran. European Curr. Research on fluid Inclusions, p.245-246 (ECROFI 2009)

[12] Roedder, E, 1984, Fluid inclusions, Reviews in Mineralogy, volumen 12, Mineralogical Society of America. .p. 644..

[13] Touret, J.L.R., 2001, Fluid inclusions in the Metamorphic racks. Lithos, v.55, p.1-25.

[14] Srikantappa, C. and Malathi, M.N., 2008, Solid inclusion of magmatic halite and CO2-H2O

Inclusions in Closepet granite from Ramanagaram, Dharwar Craton, India. Ind. Min., v. 42 (1), p.84-98.

[15] Diamond, L.W., 2001, Review of the systematics of CO2-H2O fluid inclusions. Lithos, v.55, p. 69-99.