

CO₂-H₂O, 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 región, located in SW of Mashad city in 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, muscovite, amphiboles, clinopyroxene and garnet. Base 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 are have been classified as moderately peraluminous, S to I type granitoids of sub-alkalines to calcic type.

Fluid inclusion study was caried out on Mashhad granitoids which show presence of Isolated Fluid Inclusions (IFI) as well as Trail Bound Inclusions (TBI). Based on distribution pattern of inclusions, the isolated inclusions are classified as Group of Synchronous Inclusions (GSI). Good number of fluid inclusions have been recorded in five rock types viz., grey granite, pink granite, muscovite granite, granodiorite and pegmatites exposed around Mashhad. Four types of fluid inclusions have been recorded in Mashhad granitoids viz., Type I CO₂-H₂O 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 crustal shape varying in size from 5 to 16 µm. CO₂-H₂O fluids are the most common fluids recorded in Mashhad granitoids. The volume proportion of CO₂ in CO₂-H₂O inclusions vary from 20 to 80 percent, suggesting highly varying mole fraction of CO₂ in inclusions. Minor, bi-phase, low salinity aqueous inclusions occur coeval with CO₂-H₂O inclusions. Fluid inclusion petrography and chronology of fluid entrapment data indicate the presence of Type I, CO₂-H₂O occur coeval with low salinity aqueous, represent the earliest fluids trapped in Mashhad granitoids. Presence of Type III, Halite bearing, highly saline fluids are found mainly in a quartz vein which cross cut granodiorite. Type IV, carbonic fluids occur along late fractures which cross-cut the early Type I, CO₂-H₂O fluids whihc are classified as TBI.

CO₂ in CO₂-H₂O inclusions show melting temperatures (T_m, CO₂) around -56.8 °C, indicating almost pure carbonic inclusions. T_mClath vary from 4 to 8°C. Temperature of homogenization of CO₂ into liquid phase range from - 9 to 22° C, indicating density of 0.92 to 0.68 g/cc. And the total homogenization of CO₂-H₂O inclusions range from 205 to 320°C, indicating XCO₂ values varying 0.75 to 0.20 mole fraction. The bi-phase fluid inclusions show T_m from - 5 to - 2° C with low salinity values of from 4 to 8 wt.% NaCl equivalent and temperatura of homogenization into liquid phase varying from 120 to 160°C, indicating density of 1.03 to 1.96 g/cc. Type-IV, late

carbonic inclusions show T_h ranging from 20 to 25°C with density of 0.82 to 0.78 g/cc. Type III, halite bearing fluids show temperature of melting at 315 to 335°C, indicating 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 is estimated which nearly coincide with the mineral P-T estimates. Based on micro-textural studies combined with fluid inclusion petrography, fluid present process has been inferred. There are strong evidences that indicate fluid-present partial melting process has taken place, during the formation of S-type and I-type granitoids in Mashhad area. Presence of predominantly CO₂-H₂O fluids in granodiorites as well as both CO₂-H₂O 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 low density, carbonic fluids in quartz grains are chronologically late fluids trapped in granitoids. These fluids have formed due to preferential leakage of water from the early CO₂-H₂O inclusions along micro-fractures and is related to ductile shear deformation along thrust zones in Mashhad granitoids.

1. Introduction

Presence of different types of fluids like H₂O, H₂O-NaCl, CO₂ and CO₂-H₂O and CH₄ have 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 have shown the significant role of volatiles in the generation, mobility and crystallization of granitic melts. H₂O 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 H₂O bearing fluids but also presence of CO₂, mixed CO₂-H₂O and halite bearing fluids in granitic rocks [1, 2, 3]. The origin of S- and I-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 nature and composition of fluids associated with granitic magmas but also to understand the fluid-absent or fluid present process during the formation and ascent 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 have been well documented [6,7,8,9,10]. Petrographic and few mineral chemical data has been reported on the Mashhad granite [8,9]. Except for the preliminary report of low salinity and CO₂-H₂O 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 CO₂-H₂O, low saline, highly saline and carbonic fluids in Mashhad granitoids.

2. Geology of the area

The Mesozoic Mashhad granitoid plutons (MMGP) are situated in the Binalood region located in SW of Mashhad city in NE part of Iran [6,7]. The paleo-tethys remnants consist of rocks like three types assemblage of rocks viz., (1) ophiolites consisting of peridotites, pyroxenite, isotropic gabbros, and basalts. Metacherts interbedded with thinly bedded marbles which 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 of kilometers in a NW-SE direction [7]. The granitoids have intruded the ophiolite complexes and meta-flysch during Mesozoic period [7,8]. There are two main varieties of granitoids viz., 1) S-type, continental collision / syn-collisional 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] 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 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 has been identified in Mesozoic Mashhad granitoid pluton (MMGP). The first episode of magmatism is recorded near Dehnow, where evidences of hornblende-biotite bearing tonalite and granodiorite have intruded after the first regional metamorphism before late Triassic to early Jurassic period. These rocks were classified as moderately peraluminous, S to I type granitoids of sub-alkalines to calcic type. They have also suggested that biotite bearing granodiorite exposed around Vakilabad and Kuhsangi area belong to oldest member of the granitoid suite. During the second phase of igneous activity which occurred during late Triassic period, feldspar monzogranite exposed near Sangbast area were intruded. Field and structural relations show that these intrusives are younger than granodiorite and older than 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 Triassic 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), demarcate the western margin of the Mashhad granitoids. Granitoids are relatively undeformed with the exception of ductile shears cutting granitoids near Dehnow. Near Dehnow, N-W to SE trending ductile shears with the development of mylonitic to ultramylonitic fabric is observed. These features suggest considerable reactivation along NW-SE trending thrust zone, along the western margin of the granitoids near Dehnow.

For the purpose of fluid inclusion study, based on petrography 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, muscovite, amphiboles, clinopyroxene and garnet.

Quartz show straight to lobate grain boundaries. Quartz grains show flash figures and does not exhibit undulose extinction. These features suggest that quartz grains are largely undeformed. Few quartz grains show presence of intragranular fractures. Euhedral plagioclase grains are generally fresh. They often contain euhedral grains of muscovite. In some granites, plagioclase show alteration to sericite and talc mainly in the central portions with margins of the grains free from any alteration. Flaky biotite occur between quartz and plagioclase grains and is pleochroic from brown to yellow brown. Undeformed microcline occur as tabular grains exhibiting typical cross-hatched twinning. Within the bigger microcline grains, presence of smaller, euhedral grains of twinned plagioclase is commonly observed.

Base 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.

3.Fluid Inclusions 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 orientation of fluid inclusions within the mineral into primary and pseudosecondary inclusions, following (12). 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 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 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, relative timing of entrapment of fluid inclusions have been established

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. Following three types of fluid inclusions have been recorded:

Type I CO₂-H₂O 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 crustal 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 . $\text{CO}_2\text{-H}_2\text{O}$ fluids are the most common fluids recorded in quartz grains in Mashhad granitoids. They appear bi-phase at room temperature. The volume proportion of CO_2 in $\text{CO}_2\text{-H}_2\text{O}$ inclusions vary from 20 to 80 percent, suggesting highly varying mole fraction of CO_2 in inclusions. Minor, bi-phase, low salinity aqueous inclusions occur coeval with $\text{CO}_2\text{-H}_2\text{O}$ inclusions. Fluid inclusion petrography and chronology of fluid entrapment data indicate the presence of Type I, $\text{CO}_2\text{-H}_2\text{O}$ which is the most common fluids which occur with low salinity aqueous. These Type I and Type II fluids represent the earliest fluids trapped in Mashhad granitoids. Presence of Type II, Halite bearing, highly saline fluids are found mainly in a quartz vein which cross cut granodiorite. Halite bearing inclusions are randomly distributed within the quartz grains with size 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, $\text{CO}_2\text{-H}_2\text{O}$ fluids (Fig.3). These CO_2 -rich fluids appear as dark inclusions, show negative crystal shapes to highly irregular shapes. Their size 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: 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 was 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 $\pm 0.1^\circ\text{C}$ at low temperatures and $\pm 1.0^\circ\text{C}$ at high temperatures.

CO_2 in $\text{CO}_2\text{-H}_2\text{O}$ inclusions show melting temperatures (T_m , CO_2) around -56.8°C , indicating almost pure carbonic inclusions (Table 1). $T_{m\text{Clath}}$ vary from 4 to 8°C . Temperature of homogenization of CO_2 into liquid phase range from -9 to 22°C , indicating density of 0.92 to 0.68 g/cc. The total homogenization of $\text{CO}_2\text{-H}_2\text{O}$ inclusions range from 205 to 320°C , indicating X_{CO_2} values varying 0.75 to 0.20 mole fraction [19]. The bi-phase fluid inclusions show T_m from -5 to -2°C with low salinity values of from 4 to 8 wt.% NaCl equivalent. They show homogenization into liquid phase varying from 120 to 160°C , indicating density of 1.03 to 1.96 g/cc. Type-IV, late carbonic inclusions show T_h ranging from 20 to 25°C with density of 0.82 to 0.78 g/cc. Few halite bearing type III fluids in quartz vein cross cutting granodiorite show temperature of melting at 315 to 335°C , indicating high salinity values of 38 to 40 wt. % NaCl equivalent.

4. Conclusions

Mashhad granitoids and pegmatites are largely undeformed igneous bodies intruding into meta-ophiolites and metamorphosed flysch during Mesozoic period. Mashhad granitoids are undeformed igneous bodies and show typical igneous micro-textures. Quartz grains in all the rock types studied show no signs of deformation and is considered to represent igneous

mineral. However, quartz in mylonites and ultramylonites show 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 CO₂-H₂O fluids. These fluids occur co-eval with low salinity aqueous fluids within quartz grains. The CO₂-H₂O inclusions show varying volume proportions of CO₂ indicating mole fraction of CO₂ varying from 0.75 to 0.20. In quartz veins, cross cutting granodiorite, presence of primary halite bearing fluids have 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 is estimated. Slightly lower pressure and temperature estimates obtained based on fluid inclusions study when compared to P-T data obtained based on Two-feldspar and hornblende-plagioclase thermometers is due to moderate re-equilibration of fluids probably during uplift of the granitoids. Based on these observations the primary CO₂-H₂O, 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. Presence of predominantly CO₂-H₂O fluids in granodiorites as well as both CO₂-H₂O 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 into light the significance of CO₂-H₂O 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 density (0.78 to 0.82 g/cc) carbonic fluids along intragranular fractures in quartz grains indicate that these are the chronologically late fluids trapped in granitoids. The carbonic fluids have formed due to preferential leakage of water from the early CO₂-H₂O 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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6. References

1. Konnerup-Madson, J., (1979). *Lithos*, v. 12, pp.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 Ternes, 1994. Evidence of magmatic CO₂-rich fluids in peraluminous graphite - bearing leucogranites from Deep Freeze Range. *Contrib. Mineral. Petrol.*, 117: 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 region; 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 union, 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, aleotectonic setting, metallogeny of Mashhad paleo-tetys granitoids, Iran, Denver annual meeting Colorado convention centre.
10. Iranmanesh, J. and Sethna, S.F., 1998, Petrography and geochemistry of the Mesozoic Granite at Mashhad, Khorasan Province, Northeastern 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 fluids Inclusions*, 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 rocks. *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.

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

Rock Type inclusion	CO ₂ -H ₂ O inclusions			O ₂ inclusions		H ₂ O -NaCl	
	T _m CO ₂ d _{g/cc} (GSI)	Th CO ₂	Th _{total}	T _m	T _h (TBI)	d	T _m (GSI)
Salinity (wt% NaCl equiv.)							
M-6/1 Granodiorite	-57.8	-10 to -14					
M-6/3 Pink Granite 4 to 8 120 to 160 1.03 to	-57.8	-4 to -2	255 to 290	-57.9	20 to 25	0.82	-2 to -5
						to 0.78	
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 Garnet –bearing Pegmatite	-57.8	10 to 21	260 to 295				
M-11/4 Quartz vein .	57.9 220°C	10 to 22	170 to 245		Tm of Halite vary from 205 to		

Abbreviations used in the table:

GSI: Group of synchronous fluid inclusions TBI: Total bound fluid inclusions

T_m: Temperature of melting Th: Temperature of homogenization (T_m & Th are represented in degree 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+Amp. Oldroad - Torbat. GPS – 36° 5' 12.1" E 59° 38' 47.4"

M-6/3: Pink Granite, Qz+Kfs (perthite) +Pl+Bi+Mus+Opq+Ser. GPS – 36° 5' 12.1" E 59° 38' 47.4"

M-4/1: Muscovite Granite Qtz+Kfs (perthite) +Pl+Bt+Mus, Robat Khakestar GPS– N 36° 09' 17.5" E 59° 37' 50.2"

M-5/2: Tourmaline Pegmatite, Qtz+Pl+Ms+Tur, Khakestar GPS – N 36° 06' 27.7" E 59° 38' 43.9"

M-1/1: Tourmaline Granite, Qtz+Kfs+Pl+Mus+Opaq+ Tur, Khajemorad. GPS – N36° 09' 01.4", E59° 41' 31.2"

M-6/4: Garnet –bearing Pegmatite, Qtz+Pl+Kfs+Bt+Ms+Grt+Chl+Ser, old road-torbat. GPS – N 36° 5' 12.1" E 59° 38' 47.4"

M-7/2: Garnet –bearing Pegmatite, Qtz+Pl+Kfs+Mus+Grt new road(high way). 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"

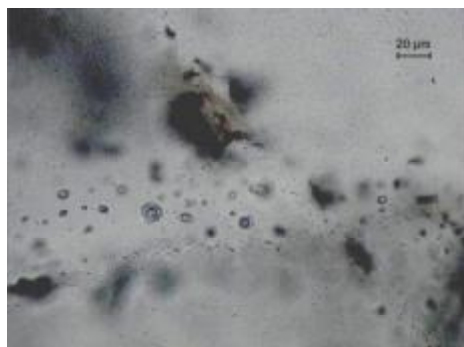


Fig. 2. Bi-phase CO₂-H₂O inclusions in quartz from Granite



Fig. 3. CO₂-rich inclusions along late fracture cross cutting CO₂ - H₂O inclusions in quartz.

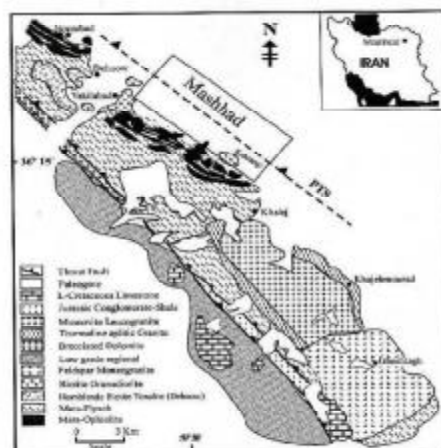


Figure 1a. Geological map of the study area. P-T-S refers to the Paleo-Tethys Suture zone.

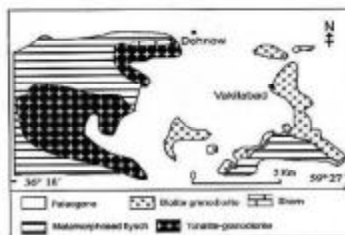


Figure 1b. Geological map showing the tonalite (Dehnow) and the gabbroite (Vakhtang). Karimpour, M.H (2005)