A study of various occurrences of the Al_2SiO_5 polymorphs in the rocks/veins of the Hamedan region, Iran: with special reference to origin of quartz-kyanite veins

A. A. Sepahi*, T. Molaee

Department of Geology, Bu-Ali Sina University, Hamedan, Iran

Abstract: The study area is a part of so-called Sanandaj-Sirjan zone or Zagros imbricate zone of the Zagros Orogen, Iran. The Hamedan region comprises a metamorphic sequence of low- to high-grade regional and contact metamorphic rocks intruded by mafic, intermediate and felsic plutonic bodies. The sequence comprises pelitic, psammitic, mafic, calc-pelitic and calc-silicate rocks. Pelitic rocks are the most abundant rocks in the region which are mostly composed of slates, phyllites, mica schists, garnet-mica schists, garnet-andalusite-(±sillimanite/±kyanite) schists, garnet-staurolite schists, mica hornfelses, garnet hornfelses, garnet-andalusite-(± fibrolite) hornfelses, cordierite-(±andalusite) hornfelses, cordierite-K-feldspar hornfelses and sillimanite-K-feldspar hornfelses. Several interlayers of amphibolites and amphibole schists alternate with pelitic rocks in the sequence. Various types of Al_2SiO_5-bearing silicic veins occur in the region. Isotope characteristics indicate metamorphic origin for some of them. In this study, we have defined three different generations of kyanite according to their various geological characteristics, including: (1) metamorphic (randomly distributed and commonly co-existed with sillimanite/andalusite), (2) stress-(shear)-induced (pseudomorphs of kyanite after andalusite in the shear zones) and (3) late-stage (hydrothermal or metasomatic) kyanites. The quartz-kyanite veins/pods are late structures that are created by interactions with wall rocks. Circulating Al- and Si-rich fluids may be responsible for formation of these veins/pods.

Keywords: *hydrothermal, metamorphic, metasomatic, kyanite, stress, veins, Hamedan, Iran.*

Introduction

In spite of earlier ideas [1, 2] considering aluminum as an immobile element, recent studies by many authors [3-8] indicate that aluminum should not be assumed to be immobile during fluid-rock interaction in deep environments. The low solubilities of aluminum hydroxides and aluminosilicates do not mean their immobility, especially in deep crustal environments [4]. The presence of segregation layers, and veins containing quartz + aluminosilicates in metamorphic environments, confirm that aluminum can be transferred from rock-forming minerals to the fluid phase and from fluid phase to Al-bearing mineralization in veins [4, 9]. Aluminum solubility increases through complexing with silica [10], alkalis [11], fluorine [12] or boron [9]. Thus, aluminum can be transported by complexes, so, in spite of its low solubility it can be mobile [4]. Dehydration reactions [13], fast release of fluid overpressure in response to rock fracturing [4] and deviatoric stress [14, 15] are possible sources of fluid-rock disequilibrium in metamorphic environments [4]. Also, there is abundant geological evidence for significant Al solubility in fluids in medium- to high-pressure geologic environments, chiefly in the form of aluminosilicate vein minerals that formed from

*Corresponding author, Telefax: +98 (0811) 8253467, Email: sepahi@basu.ac.ir

aqueous solutions during metamorphism [16-18], metasomatism and hydrothermal processes [19, 20]. Fluids may penetrate to upper crustal environments from ~~the~~ deeper levels of the crust or originate by magmatic/hydrothermal processes.

Aluminum silicate (Al_2SiO_5) polymorphs occur in a wide range of lithologies such as regional and contact metamorphic pelitic rocks, felsic (plutonic/volcanic) bodies and silicic veins [21, 22]. Although, kyanite is a common mineral of regional metamorphic terranes, the occurrence of kyanite in contact (thermal) metamorphic aureoles has also been reported by many authors [21, 23-29].

Also, in some quartz-kyanite rocks/veins, kyanite crystals may be generated by hydrothermal (and/or pneumatolytic) and metasomatic processes [19, 20, 30, 31]. The occurrence of kyanite, in the presence of a fluid phase during deformation in high strain zones as a consequence of the metasomatic reactions, has been reported, also [19, 20].

Many authors [21, 28, 32-34] have previously reported the occurrence of kyanite in the metamorphic and plutonic rocks/veins of the Hamedan region, but these authors do not indicate various generations of this mineral. In this paper, we have provided new geological features and petrogenetic data that are helpful for distinguishing various generations of kyanite in the metamorphic and plutonic rocks/veins of the region. Visible changes in color and pleochroism of various generations of kyanite occur which make their identification easy. In this study, we focus on demonstrating geological features of siliceous kyanite-bearing veins and pods and on their importance as evidence for Al mobility in natural environments (especially in metamorphic environments).

Geological setting
The study area is a part of the so-called Sanandaj-Sirjan zone or Zagros imbricate zone of the Zagros Orogen, Iran. Major metamorphic and magmatic events of the Sanandaj-Sirjan Metamorphic Belt (SSMB) have been attributed to Mesozoic age [21, 28, 34-37]. These events have been attributed by some geologists to the subduction of the Neo-

Tethyan seaway and the subsequent collision [21, 28, 34, 35].

The Hamedan region comprises a metamorphic sequence of low- to high-grade regional and contact metamorphic rocks that have been intruded by mafic, intermediate and felsic plutonic bodies (Fig. 1) [28]. The sequence comprises pelitic, psammitic, mafic, and calc-silicate rocks. Pelitic rocks are the most abundant lithologies.

Lithology of Al_2SiO_5-bearing rock units
In the region, metapelitic rocks are the most abundant rock types, and comprise slate, phyllite, mica schist, garnet schist, garnet-andalusite-(±sillimanite/±kyanite) schist, garnet-staurolite schist and garnet-sillimanite-(±kyanite) schist. Metapelitic rocks are interlayered with minor metabasaltic rocks (amphibole schist and amphibolite), metacarbonates, and calc-silicate rocks. Near the Alvand plutonic complex, cordierite – K – feldspar - (±andalusite / fibrous sillimanite) hornfelses. Garnet – staurolite - (±kyanite) hornfelses, and in some places garnet - sillimanite - (±andalusite/±kyanite) schists / migmatites with interlayers of cordierite – K – feldspar – andalusite - spinel migmatites occur.

The aluminum silicate polymorphs occur in a wide range of lithologies in the region, including regional and contact metamorphic pelitic rocks, plutonic bodies and silicic veins. Descriptions of complete sequences of the metamorphic rocks have previously been presented [21, 28, 34, 35]; therefore, we have focused our descriptions only on the Al_2SiO_5-bearing rock units. The Al_2SiO_5-bearing rocks of the region can be divided into three major categories including: Al_2SiO_5-bearing metamorphic rocks, Al_2SiO_5-bearing plutonic rocks and Al_2SiO_5-bearing vein rocks [21].

Al_2SiO_5-bearing metamorphic rocks can be sub-divided into three major rock units:
1. Regional metamorphic rocks, such as andalusite schists, andalusite-sillimanite schists and andalusite-sillimanite-(+/-kyanite) schists/migmatites.
2. Contact metamorphic rocks, such as andalusite-sillimanite hornfelses, andalusite-sillimanite-kyanite hornfelses and sillimanite hornfelses
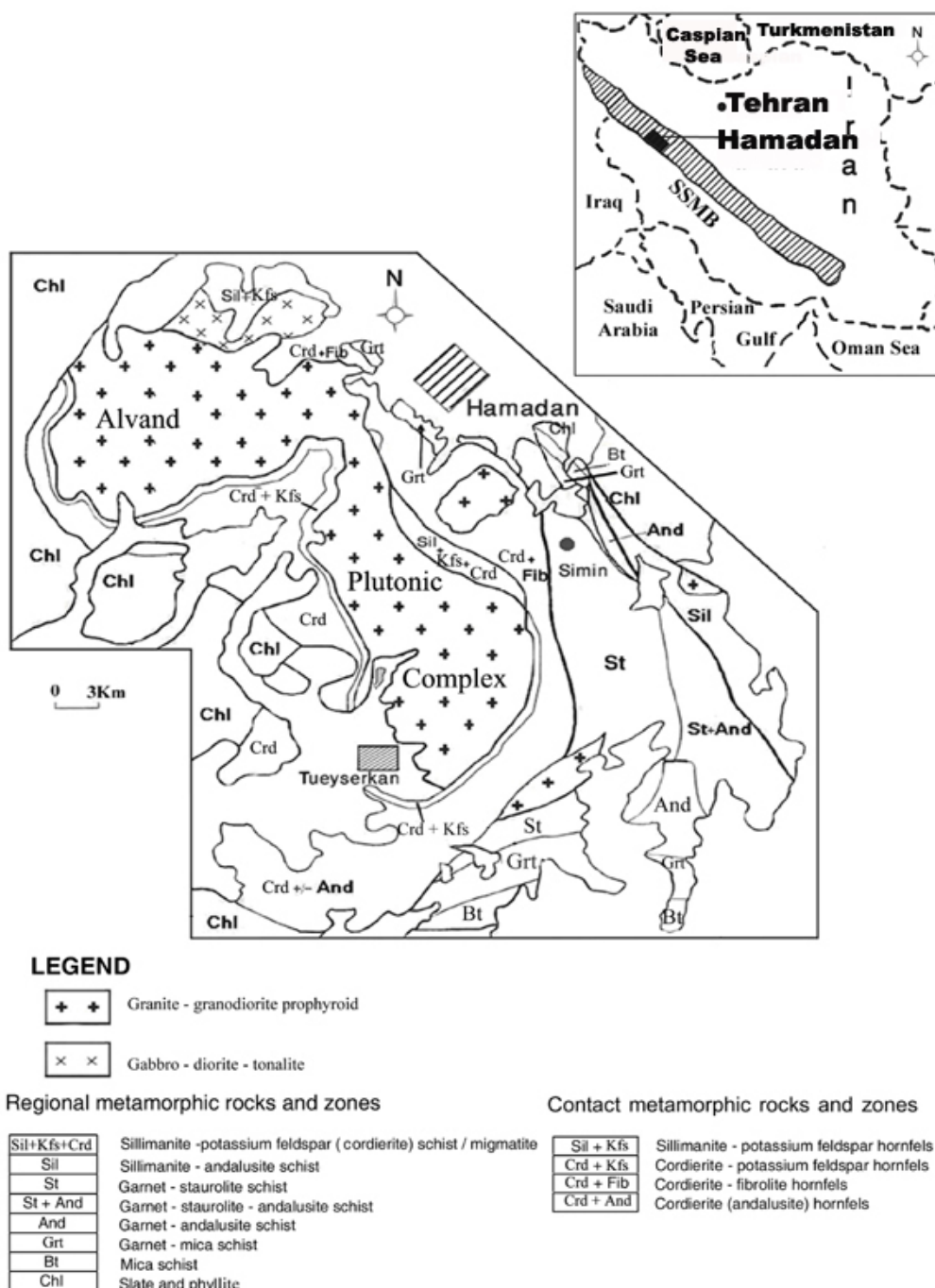3. Al_2SiO_5-bearing plutonic rocks, such as granites.

LEGEND

Regional metamorphic rocks and zones

Sil+Kfs+Crd	Sillimanite -potassium feldspar (cordierite) schist / migmatite
Sil	Sillimanite - andalusite schist
St	Garnet - staurolite schist
St + And	Garnet - staurolite - andalusite schist
And	Garnet - andalusite schist
Grt	Garnet - mica schist
Bt	Mica schist
Chl	Slate and phyllite

Contact metamorphic rocks and zones

Sil + Kfs	Sillimanite - potassium feldspar hornfels
Crd + Kfs	Cordierite - potassium feldspar hornfels
Crd + Fib	Cordierite - fibrolite hornfels
Crd + And	Cordierite (andalusite) hornfels

Figure 1 Simplified geological map of the study area. Modified after [8, 17].

Regional metamorphic rocks

Andalusite schists with porphyroblasts of garnet (up to 1 cm in diameter), and andalusite (up to 20 cm in length) have a mineral assemblage of quartz, biotite, andalusite (chiastolite), garnet, staurolite, fibrolite and muscovite. Minor minerals are graphite, plagioclase, tourmaline and ilmenite. Secondary chlorite is present.

Sillimanite-andalusite schists contain quartz, biotite, muscovite, plagioclase, and small garnet crystals (600-700   m) with large (3-20 cm long) porphyroblasts of andalusite partially replaced by prismatic sillimanite (sillimanite also occurs in these rocks as fibrolite). Accessory minerals are graphite, tourmaline and ilmenite.

High grade schists and migmatites lie adjacent to the granitic bodies in which the sillimanite / andalusite schists / migmatites alternate with minor interlayers of cordierite-bearing migmatites. The highest grade schists in the regional metamorphic sequence contain sillimanite + quartz + biotite + muscovite + garnet + plagioclase + K-feldspar (perthitic orthoclase) + ilmenite ± andalusite ± kyanite ± staurolite. These schists grade to the migmatitic rocks with the same mesosome mineralogy as the mineral assemblages of schists. These rocks are cut by abundant granitic pegmatites and aplites as well as quartz-sillimanite veins. Mesosomes of the migmatites have porphyrolepidoblastic texture and contain quartz, biotite, garnet and Al_2SiO_5 polymorphs (especially sillimanite, but in some places with andalusite and/or kyanite) ± staurolite ± spinel ± regional cordierite ± graphite (spinel in intergrowths with cordierite around sillimanite/andalusite porphyroblasts).

Contact metamorphic rocks

Rocks with hornfelsic texture, but showing primary regional metamorphic assemblages, such as staurolite, andalusite, and kyanite, are common in the region. Minor amounts of texturally-late cordierite and fibrous sillimanite occur in these rocks (hornfelsed schists). Rocks in the inner contact zone include cordierite-andalusite-garnet hornfels, cordierite-K-feldspar-(±garnet) hornfels and sillimanite-K-feldspar-(garnet) hornfels.

Kyanite-bearing schists occur at scattered localities within other zones (Fig. 2). They contain biotite + plagioclase + quartz + kyanite ± garnet. Kyanite-quartz veins (containing minor muscovite, chlorite, and ilmenite) cut through various lithologies in the regional metamorphic sequence and the thermal metamorphic rocks near contact zones of the plutons. In the veins, muscovite and chlorite are commonly retrograde, as is minor diaspore. Some kyanite schists/hornfelses in the contact zone have textures indicating two distinct generations of kyanite. In these rocks, some kyanite crystals are deformed. These rocks also contain idioblastic, randomly oriented kyanite that is typically less tabular than the broken kyanite which cross-cuts the relict foliation and occurs in the vicinity of quartz-kyanite veins. Typical mineral assemblage of host rocks of quartz-kyanite veins (hornfelsed schists near the wall zone) is quartz + biotite + andalusite + sillimanite

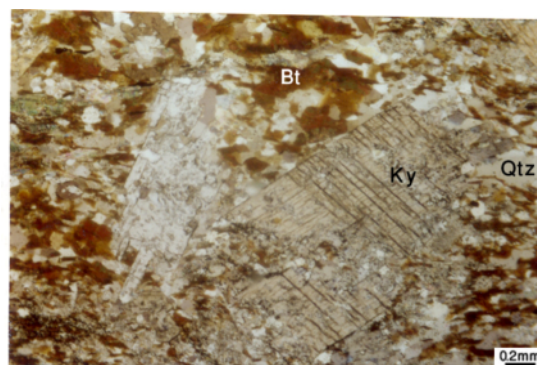(fibrolite) ± garnet, ± cordierite, ± muscovite (kyanite and muscovite are late stage minerals).

Figure 2 Photomicrograph (ppl) of a kyanite-bearing schist from the study area (length of kyanite crystal is about l mm).

Plutonic rocks containing Al_2SiO_5 minerals:

Plutonic rocks of the Alvand (Hamadan) complex can be divided into three categories: gabbro-diorite-tonalite (GDT) association, monzogranite-granodiorite porphyroids, and hololeucocratic granitoids (leucogranite to leucotonalite). The granites-granodiorites, which mostly have a porphyritic texture, contain feldspars (plagioclase (~20-25 modal %), orthoclase (~15-20 modal %) and minor microcline (~5 modal %)), quartz (~25-30 modal %) and biotite (~27-30 modal %; rarely muscovite); minor tourmaline, apatite and zircon without any hornblende as a mafic mineral. Restites and xenocrysts of the Al-silicates are typical enclaves in monzogranites and granodiorites of the Alvand plutonic complex. Xenocrysts of andalusite, sillimanite, garnet and cordierite are common in these rocks. In the region, the xenocrysts of Al-silicate minerals were generated due to mechanical dispersion of the Al-silicate-bearing enclaves (such as xenocrysts of andalusite, sillimanite, garnet and pinitized cordierite) or resulted from disaggregation of the pieces of schists and migmatites incorporated in the granitic magma during its ascent and emplacement.

On the basis of classification schemes of [22, 38], the observed andalusite xenocrysts in monzogranites have exogenic (metamorphic) origin. The existence of disequilibrium textures at the contact between the andalusite xenocrysts and their granitic/dioritic hosts of the Alvand plutonic complex (also alongside cleavage planes of the andalusite xenocrysts; Fig. 3a-b), indicate that they should not have crystallized from granitic/dioritic melts. The presence of andalusite and/or

sillimanite xenocrysts, in peraluminous granitic rocks and the metaluminous dioritic rocks, confirms that most xenocrysts have been formed by disaggregation of country rocks, such as andalusite-sillimanite-bearing schists and migmatites, during intrusion and emplacement of the plutons.

Typology of the Al_2SiO_5-bearing rocks and veins/pods

Sepahi et al. [21] have reported the occurrence of various Al_2SiO_5-bearing veins in the region, including andalusite-bearing veins, andalusite-kyanite-bearing veins, andalusite-sillimanite-bearing veins, andalusite-kyanite-sillimanite-bearing veins, kyanite-bearing veins, sillimanite-bearing veins and sillimanite-kyanite–bearing veins. Oxygen isotopic data (Table 1; $\delta^{18}O$ = 14-17) are consistent with a metamorphic origin for the Al_2SiO_5 minerals and quartz, and accordingly for fluids which generated these minerals.
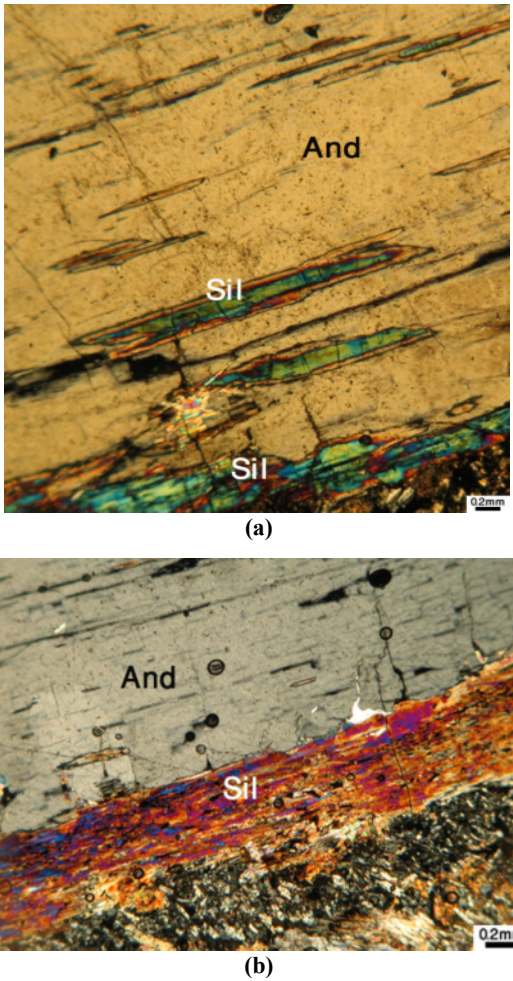

(a)

(b)

Figure 3 Examples of partial replacement of andalusite, from rims and cleavage planes, by sillimanite (xpl).

Table 1 The representative amounts of the oxygen isotope ratios, for quartz and Al_2SiO_5 minerals from veins of the Hamedan area. Data were obtained using a ICP-MS, Finnigan-MAT 251 model, using BrF_5 reagent and 32 W CO_2 laser, at the University of Wisconsin. The precision of the analyses has been nearly 0.05-0.12 ‰, examined with garnet standard sample of UWG-2 with $\delta^{18}O$=5.8, in comparison to SMOW. ** = average of 5 samples, * = average of 2 samples.

Samples	And-Ky-Vein *	Sil-Ky-Vein **	And-Sil-Vein *
$\delta^{18}O_{Qz}$	17.08	16.90	16.83
$\delta^{18}O_{And}$	14.19	-	14.52
$\delta^{18}O_{Ky}$	14.12	14.41	-
$\delta^{18}O_{Sil}$	-	14.14	14.57

Kyanite bearing veins/pods

Quartz-rich kyanite-bearing veins/pods cut through various rock units in the Hamedan region, including regional and contact metamorphic rocks, and granitic rocks (Fig. 4a-d). Preferred orientation of the veins is approximately parallel to the structure of the host rocks, and also, to the general trend of regional structures (i.e., NW-SE trend). The thickness of veins and pods vary from less than a few centimeters to more than several meters. In most places, the kyanite crystals have grown at right angles to the rock-vein interfaces and/or to the strike of the veins (Fig. 4b, d).

Major characteristics of various generations of kyanite in the veins/rocks

In this study, we have divided the kyanite crystals of the various rocks in the region into three distinct generations (Table 2) including: (1) Regional /contact metamorphic, (2) Stress (shear)-induced (dynamo-metamorphic) (3) late-stage (hydrothermal or metasomatic kyanite?).

Regional/contact metamorphic kyanite has not crystallized at the expense of andalusite porphyroblasts. Shear-induced kyanite crystals occur as pseudomorphs of kyanite after andalusite porphyroblasts developed in the shear zones. Late-

stage kyanite crystals occur in the late-stage quartz-kyanite veins/pods cutting through metamorphic and plutonic rocks near contact zone, at right angles to the vein strike.

Color, pleochroism and zoning in the observed kyanite crystals: The link between the chemical composition and intensive change in color and pleochroism of kyanite has been studied by some authors, previously. The presence of minor amounts of Cr^{3+}, Ti^{3+}, Ti^{4+}, Fe^{2+} and Fe^{3+} in kyanite may intensively affect the color of this mineral. White and White [39] have attributed the blue color of kyanite to the presence of trace amounts of Ti^{3+}, but many authors [40-43] have attributed this color of kyanite and some other minerals to the $Fe^{2+} \rightarrow Fe^{3+}$ transfer process. Also, the published analyses of kyanite by many authors have not supported the importance of titanium concentration in generating the blue color of kyanite [44-47]. When an apparent correlation occurs between titanium concentration and the blue color of kyanite, the titanium may be present as Ti^{4+} rather than Ti^{3+} and the cationic couple of $Fe^{2+} + Ti^{4+}$ can be more common than $Fe^{3+} + Ti^{3+}$ in the kyanite lattice [46, 47].
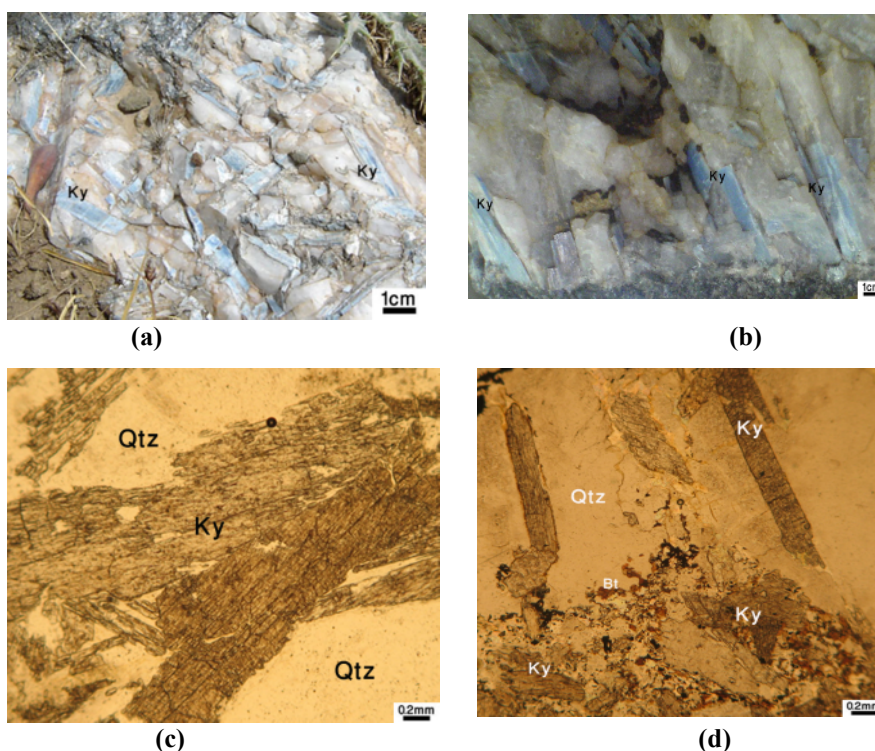

Figure 4 a-b) Outcrops of quartz-kyanite veins in the study area (maximum length of observed crystals in the photos is about 5 cm), c) photomicrograph (ppl) from a quartz-kyanite vein of the study area, d) photomicrograph (ppl) from a quartz-kyanite vein and its nearby kyanite-rich hornfelsed schist from the study area.

Table 2 Summary of major characteristics of various generations of kyanite crystals from silicic veins of the Hamedan region, Iran.

Distinguishing criteria/Generation	Generation 1	Generation 2	Generation 3
Common color	Moderate blue	Pale blue to white (commonly unzoned)	Deep blue to greenish blue (commonly zoned)
Host rocks	Pelitic schists	Pelitic schists / migmatites	Various (e.g. hornfels, granite and schist)
Mineral assemblage	Qtz, And, Sil, Ky, Grt, Bt, ($\pm$ St $\pm$ Ms)	Qtz, And, Ky, Grt, Bt, St, Ms	Qtz, Ky $\pm$ Ms $\pm$ Chl
Origin	Regional metamorphism	Stress (shear)-induced	Late-stage (hydrothermal ?)

Discussion and concluding remarks:

Although, the existence of kyanite-bearing rocks and veins has already been reported from the Hamedan region [21, 28, 32, 33, 34, 35], the major problems in regard to occurrence and origin of kyanite in these rocks and veins still remain unresolved. In many places in the Hamedan region, the relationships of the kyanite crystals in the veins indicate that kyanite may have crystallized by fluid-rock interactions (i.e., many kyanite crystals occur at right angles to the main trend of the veins (Fig. 4b) and/or host rock structures such as bedding or schistosity planes), although fluids may be provided from an external source. Examples of such veins/pods, in medium-high grade metamorphic rocks, containing quartz and Al_2SiO_5 polymorphs have been reported by many authors [9, 16, 17, 21, 23, 48-55].

The chemical composition of the host rocks and the presence of stress can be essential factors in regard to the crystallization of some generations of kyanite. The possible effect of stress, induced by tectonic features, such as shear zones, on the formation of kyanite or inversion of sillimanite/andalusite to kyanite has been reported by some authors [56-60]. In the Hamedan region porphyroblasts of andalusite/sillimanite have been altered to kyanite in shear zones (e.g., south of Simin area).

In the Hamedan region, the occurrence of some quartz-kyanite veins near the contact zone of the granitic intrusions and the observation that these veins cut through the intrusions at the several outcrops, confirm a possible hydrothermal origin for the veins. The source of Al and Si, however, the mechanism of the production of large volumes of Si and Al for generation of voluminous aggregates of quartz and kyanite, crystallized in situ and perpendicular to the wall zone of many veins by interaction with wall rocks in an advective fluid model remains problematic. It is possible that circulating fluids have leached Al from Al-rich rocks and deposited it in different lithologies (i.e., Al has been leached from Al-rich lithologies but not necessarily deposited in veins cutting through Al-saturated rocks). This possibility means that it is better to consider a circulating-fluids model in contrast to a common advective-fluids model (which has been suggested for generation of Al_2SiO_5-bearing veins/pods [4]).

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