اولین همایش ملی گوهرشناسی و کانی های صنعتی
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Gem Andradite Garnet Deposits (Demantoid Variety) of Kerman:

Geology, Mineralogy and Genesis

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Abstract

In order to reveal the formation mechanism of different garnets from the Kouh Gabbri area (SE Iran), a geochemical, mineralogical and gemological study applied XRD, XRF and ICP-MS on gem quality demantoid garnets. Crystals of demantoid with green to yellowish-green color, crystal clusters and single crystals as large as 10–20 mm (most range from 2 to 10 mm in diameter) have been observed in the study area.

The deposit is characterized by magnetite and hematite concentrations with distinctly low chromium contents (<0.03 Cr_2O_3) and contain Cu sulfide minerals (e.g. chalcopyrite).

Because of the large-scale intergrowths, the Kouh Gabbri samples contain four different compositions. First one, pure andradite (Adr>95) associated with sulfide stage, and second one, Al-rich andradite, formed at the early stage of amphibole-epidote-heamatite stage and third one, a solid solution between grossular and andradite. In the final stage, grossular, formed at Ca-silicate stage. Trace elements element contents as well as Mg, Mn, Ni, Cr, Co, Zn and La values demonstrated in obtaining accurate origin information for the samples. They revealed that demantoids from the study area have a relatively low lithium content (< 200 ppm) compared to demantoids from other places (>250 ppm). Demantoid garnets from the study area, do not contain Cr^{3+}, and their color is attributed to the presence of Fe^{3+} in the octahedral sites.

Keywords: Demantoid garnet, Kouh Gabbri, octahedral sites

Introduction

Garnet is a common rock-forming mineral in igneous and especially characteristic of -metamorphic rocks of a wide variety of types (Deer et al., 1996) and a major associated gangue mineral in different types of skarn or associated deposits (Meinert et al., 2005). Hydrothermal garnets in skarn type or associated deposits can be divided into Pyralspite (pyrope, almandine, spessartine) and Ugrandite (uvarovite, grossular, andradite) groups (Grew et al., 2010). Generally, hydrothermal garnets in skarn-type are in the grossular andradite solid solutions (Fei et al., 2019). The formation of hydrothermal garnet is controlled by fluid-rock interaction, fluid temperature, oxygen fugacity, fluid flow rate, pH, and chemical compositions (Park, 2017).

The minerals of the garnet group have the general chemical formula $X_3Y_2Z_3O_{12}$, where X is usually Ca^{2+}, Mn^{2+}, Fe^{2+}, and/or Mg^{2+}; Y is generally Al^{3+}, Fe^{3+}, Cr^{3+} and/or V^{3+}; and Z is commonly Si^{4+} (Antao, and Klincker, 2013).

Andradite, (a calcium-iron garnet sometimes with some Al, Cr, or Ti replacing some iron), is typically found with grossular in contact-metamorphosed limestone. It has a variable formula $Ca_3(Fe^{3+}, Al, Cr, Ti)_2Si_3O_{12}$ and theoretical composition of 35.47 wt% SiO_2, 31.42 wt% Fe_2O_3 and 33.11 wt% CaO. Andradite crystallizes in the cubic system (space group $Ia\bar{3}d$. The colors of andradite garnet varieties are in the brownish-green to brown, reddish-brown, bronze, orange, yellow, deep green (demantoid), gray, and black. Occasionally andradite is iridescent and multicolored with streaks of brownish yellow, reddish-brown, and black.

Because of the large-scale intergrowths, samples from Iran contain 3 different compositions, $Adr_{86}Uv_{12}$, $Adr_{69}Uv_{30}$, and $Adr_{76}Uv_{22}$. (Antao and Klincker, 2013). The three different cubic phases in each sample cause strain that arises from the mismatch of the cubic unit-cell parameters and give rise to birefringence. The dominant phase for each sample has the following unit-cell parameters (Å) and weight fractions (%): 12.05962(2), 63.3(1) (Antao and Klincker, 2013).

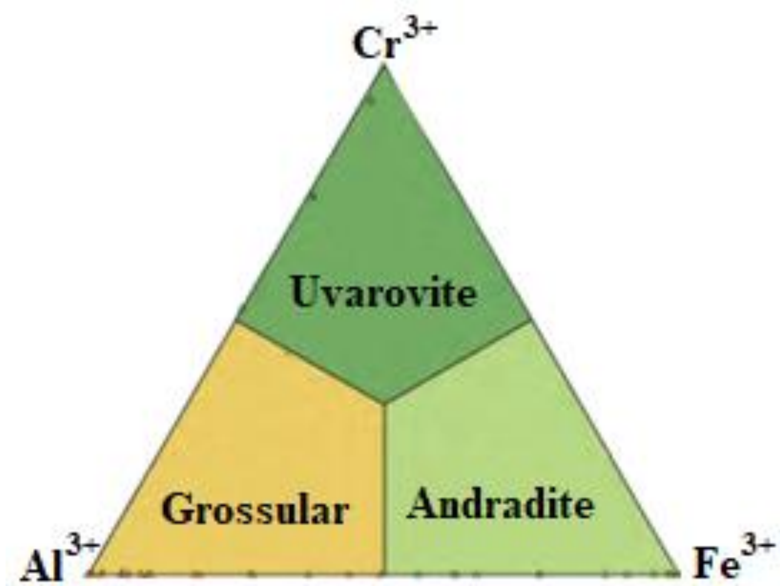

Fig. 1. Chemical ternary diagram Cr^{3+} -Fe^{3+} -Al^{3+} of the ugrandite series.

Demantoid is the green variety of andradite (with an ideal formula [$Ca_3(Fe^{3+}, Al, Cr, Ti)_2Si_3O_{12}$] transparent to translucent with an adamantine to resinous luster. Demantoid is colored by chromium and/or vanadium (iron may also contribute to the color). Demantoid of gem quality is not always formed because many parameters play important roles in gem formation. Importantly, post-growth phenomena that might damage the gem, such as mechanical fracturing, chemical etching, etc., should be absent (Groat, and Laurs, 2009).

In 2001, demantoid garnet from Iran was discovered in Kerman province in the southeast of the country (Du Toit et al., 2006). Demantoids of different parts of Kerman area (Baghin, Kouh Gabbri, Bagh Borj, Soghan, Gol Gohar, Kouh Tanbor, Khajoo), show wide ranges of physical properties and chemical compositions. In this study, we carried out a Comprehensive study of garnet mineralogy as well as major and trace element compositions of garnet from different stages to discuss genesis of mineral deposit by trace elements and REE substitution mechanismconditions and change in garnet composition at different stages.

Geological Setting of the Deposit

The study area is located in the southeastern part of Iran, southeastern of Rafsanjan (Kerman province). The geology of the study area is dominated by the exposure of the limestone and calc-alkaline granitoid.

The Kouh Gabbri is located in the south eastern Mountains of Rafsanjan in the central south Iran. The major faults and folds in the area are showing a NW- SE trend. The skarn garnet deposits in the area occur along the contact zone between the Kouh Gabbri granite and Cretaceous to Paleocene limestones. The Kouh Gabbri pluton is dominated by granite and alkali granite (Abedpour, et al., 2013) which intruded Cretaceous to Paleocene limestones and conglomerates (Nouri et al., 2021).

Skarn deposits are primary sources of Fe, Cu, Pb, Zn, W and Mo, and are commonly generated through interaction between high-temperature magmatic-hydrothermal fluids and carbonate rocks. In the ore-forming process, the magmatic-hydrothermal fluids transport ore metals into carbonate rocks, and cause contact metamorphism and metasomatism of the host carbonate rocks (Meinert et al., 2005). Skarns are developed along the contacts of the porphyritic granite and limestone (marble) and show visible zonation. Deep green garnet is developed proximal to porphyritic granite, green garnet is developed in the intermediate, and pale green garnet is developed adjacent to limestone rocks.

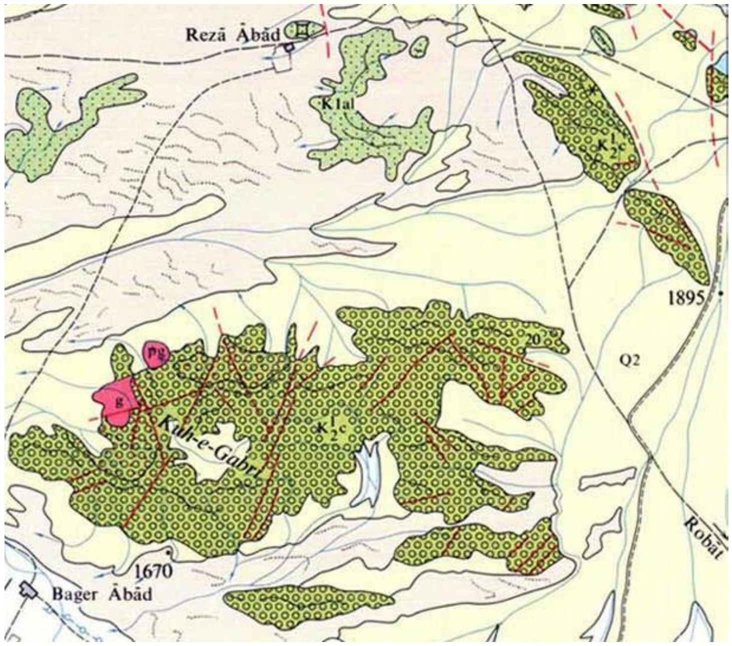

Fig. 1. Simplified geologic map of the Kouh Gabbri complex.

Materials and Methods

From the study area, 15 representative samples collected. Optical microscopy, XRD and SEM-EDS analysis of samples are used to characterize mineral assemblages and alteration types. Fresh samples were slabbed, reduced to 0.7 cm sized pieces, and crushed in a steel jaw-crusher. The powder was analyzed for major and trace elements by XRF and ICP -MS methods. Sampled garnets in this study were collected from different stages and regions and examined by XRD, XRF and ICP-MS methods. Twenty samples were collected for mineral identification by X-ray diffraction (XRD). Samples were crushed, powdered, and sieved to <0.125 mm grain size. Samples were analyzed from 3 to 75° 2θ at 2° 2θ/min, with Cu–Kα radiation.

A total of 3 samples from the deposit were analyzed for their major, minor, trace and rare elements compositions. The major elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, MnO, CaO, Na_2O, K_2O, P_2O_5) and trace elements (Pd, W, Co, Cr, Bi, Rb, Sn, Sr, As, Sb, Ag, Cd, Th, U, V, Pt, Zr, Ni, Mo, Rh), were determined by XRF. Rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), were measured by ICP–MS technique.

From the study area, 15 representative samples collected. Three representative samples were cut into thin cross-sections. Detailed mineralogical and gemological studies were carried out using petrographic microscope and gem microscope.12 samples were partially ground into powder with a grain size under 200 mesh for geochemical analysis.

Results and Discussion

Garnet mineralogy

Based on mineralogical studies, garnets from the Kouh Gabbri can be divided into 4 different compositions. Type 1, pure andradite (Adr>95) associated with sulfide stage. Type 2, Al-rich andradite, formed at the early stage of amphibole-epidote-heamatite stage. Type 3, a solid solution between grossular and andradite. Type 4, grossular, formed at Ca-silicate stage. The XRD experimental data, showed that the main component of the garnet is andradite. The associated minerals include magnetite, quartz, calcite, and wollastonite.

Most of the samples studied had a green or deep green homogenous color. Under PPL light, the garnet grains show euhedral to subhedral granular structure with positive high relief. Due to changing physicochemical conditions, garnets in the study area display variations in texture and composition. The garnet in the skarn deposit ranges in size from 0.01 to 30 mm. The measured density ranged from 3.78 to 3.92 g/cm^3, average = 3.85.

Chemistry of Garnets

The chemical compositions of demantoid garnets in the study area, were investigated for major and trace elements by XRF and ICP-MS. The Kouh Gabbri garnets have zoning characterized by relatively low alumina contents, up to 0.05 wt% of Al_2O_3. For Kouh Gabbri garnet, Cr and V were not detected and only 15 ppm of Cr and less than 11 ppm of V were measured by ICP-MS. The main trace elements are Mg up to 300 ppm and Mn up to 700 ppm.

The Cr ranges from 4 to 691 ppm in the green, brown and yellow colored with highest values of 15,347 ppm in deep green colored varieties. Each occurrence has both unique mineral assemblage and trace element chemistry (with variable Fe/Mg, Ga/Mg, Ga/Cr and Fe/Ti ratios). Kerman garnets are characterized by wide color variation, homogeneity of the color hues, and transparency, and can be considered as a potential gemstone.

Table 2. The chemical analysis of Kerman garnet deposit.

	SiO_2	Al_2O_3	TiO_2	MgO	MnO	CaO	Na_2O	K_2O	Fe_2O_3	P_2O_5	LOI
Kerman garnet	36.99	0.05	0.02	0.04	0.10	31.73	0.01	0.01	30.17	0.01	0.82

The garnet deposit was formed at the contact zone between granitic magma intrusion and limestone. Hydrothermal solutions derived from the magmas rich in Si, Al, and Fe react with Ca and Mg-rich limestone forming a skarn rock in a metamorphic process. Mineralization in the study area, is characterized by faulting, fracturing and fluid-rock interactions due to the intrusion of granitoid magmas into limestone rocks. The skarn process shows 3 stages of formation. First, in contact metamorphism of the limestone-granitoid with the formation of fine-grains of grossular. Second, high fracturing and third, hydrothermal metasomatism related to fluid circulation, which heated the surrounding limestone rocks and changed their whole chemical composition. Different garnets collected from the study area have varying trace element contents. The Type 1 garnet has the highest Ti, V, Sc, Ga, Nb and Th contents.

Type of Deposit

Most economic garnet deposits are associated with skarns and serpentinized ultramafic rocks (Adamo et al., 2011; Barrois et al., 2013). In the study area, due to the intrusion of granitoid into limestone, huge hydro-fracturing in the wall rock occurred and calcic silicate minerals such as wollastonite, diopside, vesuvianite, calcite and quartz, formed during fluid-rock interactions.

Table 1. Main geological and mineralogical characteristics of demantoid garnet deposits of Iran.

Deposit	Kouh Gabbri	Bagh Borj	Takab
Type of Deposit	skarn	Serpentinites	skarn
Genetic Model	M-HM	MM	M-HM
Formation and/or Series	Alkaline granitoid intruding the Mesozoic sedimentary formation	Haji-Abad ophiolites Zagros ophiolites belt	Alkaline granitoid intruding the Mesozoic sedimentary formation
Host Rock	metamorphic skarn hydrothermal skarn	serpentinites asbestos lenses	metamorphic skarn hydrothermal skarn
Wall Rocks	Limestone, conglomerate	asbestos rocks, talc rocks, serpentinites	Limestone,
Mineralization Control	hydrothermal metasomatism, fractures, veins, pockets	disseminations, fractures	hydrothermal metasomatism, fractures, veins, pockets
Typical Mineral Assemblage	wollastonite, epidot, andradite, grossular, calcite, quartz, hematite, vesuvianite	asbestos, serpentine, Cr-magnetite, chromite antigorite, chrysotile	calcite, diopside, quartz sphalerite, topazolite, prehnite, wollastonite

Metamorphism		P and T = unknown	P and T = unknown	P and T = unknown
Age of the Mineralization		Alpine-Himalayan orogeny Cenozoic	Alpine-Himalayan orogeny Cenozoic	Alpine-Himalayan orogeny Cenozoic
Chemistry of Garnet	Cr_2O_3	0.002 – 0.03	*0.01 - 9.1 (wt. %)	
	Fe_2O_3	30.17	*23.78 - 31.69 (wt. %)	
	Al_2O_3	0.05	*0.01 - 0.15 (wt. %)	
$\delta^{18}O$ andradite (‰, V-SMOW)		-	$4.7 < \delta^{18}O < 6.2$ (n=3)	

* Barrois et al. (2013)

Conclusion

The skarn garnet deposits in the area occur along the contact zone between the Kouh Gabbri granite and Cretaceous to Paleocene limestones but the Bagh Borj demantoid garnet deposit is associated with metamorphosed ophiolites. The skarn process shows 3 stages of formation. First, in contact metamorphism of the limestone-granitoid with the formation of fine-grains of grossular. Second, high fracturing and third, hydrothermal metasomatism related to fluid circulation, which heated the surrounding limestone rocks and changed their whole chemical composition. Different garnets collected from the study area have varying trace element contents. The Type 1 garnet has the highest Ti, V, Sc, Ga, Nb and Th contents.

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