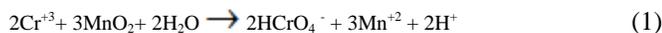


B. Hydrogeochemical processes governing the origin and transportation of Cr(VI) in Water

Hydrogeochemical processes are governing the origin, Chemical evolution transport and fate of Cr(VI) from ophiolitic complex and mineralized rock to surface and groundwaters in the area. Water samples acquire the dissolved solids by reaction of meteoric waters with the minerals in the bedrock. DO and pH are important factors affecting the physical and the presence of chromium species. The concentration of Cr(VI) in water with pH > 7.5 and DO > 0.5 mg/l, is higher than that of Cr(III) [2]. With increasing pH, Cr and other trace elements adsorbed onto Fe oxides and Mn, are released into the solution [20]. Cr(III) is highly concentrated in areas where the dissolved oxygen content of less than 1 mg/l and a pH is in the neutral range [26]. Cr(VI) has direct relationship with DO. From thermodynamically view, Cr(VI) is stable in high concentrated oxygen environment [20]. In the case of the studied ophiolite, the amount of pH > 7.9 and DO is greater than 7.67 mg/l. These values indicate that the soluble chromium is more Cr(VI). In neutral conditions, redox potential of Cr, is directly affected by Mn and oxygen of water content [6]. According to the (1), coating insoluble manganese oxides on soils and sediments in the saturated zone is a transformation factor of Cr(III) to Cr(VI):



As Cr(VI) adsorbed by cations such as Mn and Manganese compounds are important absorbent of Cr, it can be deduced that the chromium in water resources must contain significant amounts of Cr(VI) and is in the form of chromate (CrO_4^{2-}).

C. The distribution of major elements in water resources

Dissolved cations in studied waters are released through geochemical weathering processes. The most abundance of ionic compositions can be described as Na^+ , Ca^{2+} , Mg^{2+} , K^+ cations and Cl^- , HCO_3^- and SO_4^{2-} anions trend. The groundwater–mineral interactions in aquifer play an important role in water quality and groundwater contamination. In addition, to investigating the origin and concentration of elements, the concentrations of cations and anions were compared with World Health Organization standards.

Sodium (Na^+): The dominant cation in the stream waters of the study area is Na^+ . The average value of Na^+ in studied samples is 279.1 ppm. The Lowest sodium concentration was found in the sample No 5 (23 ppm), but the highest value was in the sample No 4 (713 ppm). The desirable amount for human consumption is 50 ppm [38]. The main source of sodium in waters is associated with evaporite deposits which their outcrops in the southern mountains of the study area are visible.

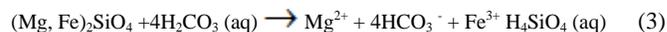
Calcium (Ca^{2+}): Calcium in waters of studied area varies from 30 to 138 ppm with the mean of 74 ppm (Table II). The desirable and permissible limit of Ca^{2+} in the drinking water is 75 and 200 ppm [38]. It implies that the drinking water in the study area is within recommended value. The main source of calcium in the area is associated with carbonatic rocks. An extensive outcrop of carbonates in the margins of ophiolitic unit is exposed in an east-west trending belt in the southern part of the Fariman - Sabzevar ophiolite complex. Water samples acquire the dissolved calcium by reaction of meteoric

waters rich in CO_2 with saussurized plagioclases and ferromagnesian minerals containing calcium of gabbroic, diabasic and basaltic units in the bedrock. For example, the interaction of labradorite in the gabbro, diabase and basalt units in the study area can be expressed as follows (2) [22]:



The effect of waters containing CO_2 on igneous minerals for the production of clay minerals and soluble ions (Ca^{2+} , Na^+ and HCO_3^-) is shown in this equation. The instability of Ca-silicates leads to an increase the Ca^{2+} in the fluids along with an increase in pH. Therefore, waters discharging from serpentinites have high pH and are rich in Ca^{2+} .

Magnesium (Mg^{2+}): The third cation in the water samples of the study area is Mg^{2+} . The average value of Mg^{2+} in studied samples is 56.7 ppm. The Lowest sodium concentration was found in the sample No 6 (24 ppm), but the highest value was in the sample No 4 (117.6 ppm). Up to 50 ppm Mg^{2+} concentration in drinking water is considered safe for human health [38]. The presence of CO_2 , Fe and Mg^{2+} catalysts, associated with H_2O create conditions favorable for the serpentinization of ferromagnesian minerals (olivine, pyroxene and amphiboles). Serpentinization of olivine in peridotite and its interaction with H_2CO_3 , can be described as [12]:



The source of magnesium ion in the area can be determined from the ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$. If the ratio is less than 0.7, the origin of Mg^{2+} is from limestones, in the range of 0.7 to 0.9 dolomitic, but if it is greater than 1, the origin of Mg^{2+} is from ophiolitic rocks [17]. As the ratio is higher than 1, therefore, a source of ophiolitic complex can be considered for magnesium ions. The carbon - oxygen isotope data was revealed that the origin of Mg^{2+} in magnesites was related to ultramafic host rocks during serpentinization reaction time [1]. Therefore, The instability of Mg-silicates leads to an increase of Mg^{2+} in the fluids along with an increase in pH. Therefore, low-temperature fluids discharging from serpentinite-hosted rocks have characteristically high Mg^{2+} .

Potassium (K^+): In contrast Na^+ the amount of K^+ in studied samples is very low (average 11.7 ppm). The amount of K^+ is in safe limit, set by the WHO. The desirable limit of K^+ in the drinking water is 12 ppm [38]. Low levels of potassium in comparison with other cations in the region are related to the lack of potassium-bearing minerals in ophiolitic complex, its greater resistance to chemical weathering and substituting in the crystal structure of some clay minerals [36].

Bicarbonate (HCO_3^-): HCO_3^- as the dominant anion in the water samples of study area ranged between 183-543 ppm. The mean value (355 ppm) of HCO_3^- ions is less than maximum permissible limit (120 ppm) [38] in the waters of study area. An important factor in creating the bicarbonate ion is related with alteration of ferromagnesian silicates and plagioclase (based on the interaction of 2 and 3). Due to the significant bicarbonate anion in waters of the area, the probable origin is weathering of silicate minerals (such as olivine and plagioclase) [11].

Chloride (Cl⁻): The chloride concentration in the groundwater of the study area ranged 44.9-862.5 ppm. The amount is higher than desirable limit (250 ppm) [38]. Serpentinite as carriers of chloride in subduction zones have high levels of chlorine [5]-[32]. Chlorine is present in two forms in serpentinized rocks [36]. In addition, the main source of Cl⁻ in waters is associated with evaporite deposits which their outcrops in the southern mountains of the study area are visible.

Sulfate (SO₄²⁻): The values range from 52.8 to 715 ppm with a mean concentration of 294.8 ppm. WHO [38] has established 200 and 600 ppm as desirable and permissible limit in the drinking water respectively. The main source of SO₄²⁻ in the area can be related with evaporite deposits in the southern mountains of the study area.

V. CEMICAL PROSESSES AFFECTIN WATER

Gibbs diagram [14] has been used extensively in water resource studies to understand hydrochemical trends. The diagram provides a simple tool to identify waters that are dominated by rock weathering, evaporation-crystallization or precipitation. In order to evaluate the effect of hydrochemical processes, Gibbs diagram was used. Waters affected by high evaporative deposits are generally expected to present high TDS and Na⁺/Ca²⁺ + Na⁺ ratios. Most of points in the diagram fall between the regions, which indicate rock weathering. According to Gibbs diagram Fig. 3., it can be deduced that the weathering of abundant ferromagnesian minerals in ophiolite complexes have a significant impact on local water chemistry in the environment.

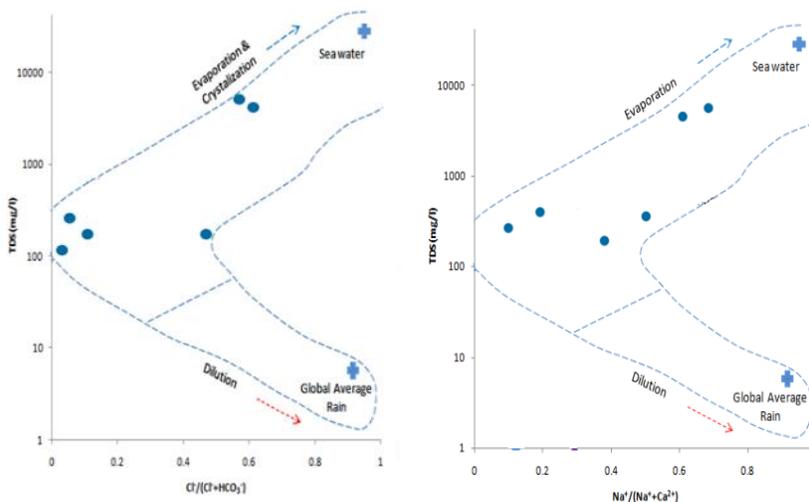


Fig. 3 Location of water samples on Gibbs Models

Diagrams of $[Na^+ + K^+] / [HCO_3^-]$ versus $[HCO_3^-] / [Ca^{2+} + Mg^{2+}]$ which are based on chemical stoichiometry [15], may indicated the origin of the dissolution of minerals in water (Fig. 4). The weathering process deduced from water situations on the above diagram. The $[HCO_3^-] / [Na^+ + K^+]$ ratio (0.1-1.5), indicating the dissolution of Na⁺ and K⁺ bearing minerals in the study area . These points can also be deduced

from $[HCO_3^- + SO_4^{2-}]$ anions ratio to $[Ca^{2+} + Mg^{2+}]$ cations. The above ratio in water samples are always higher than 1 (about 1.2) which indicates the necessity of dissolution of minerals containing Na⁺ and K⁺ cations (in the ionic balance) between cations and anions in water samples.

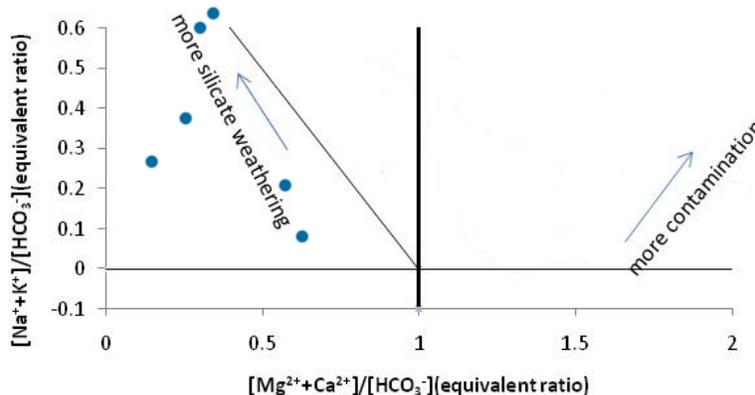


Fig. 4 Location of water samples on $[HCO_3^-] / [Na^+ + K^+]$ versus $[HCO_3^-] / [Ca^{2+} + Mg^{2+}]$

Diagram of $\text{Ca}^{2+}/\text{Mg}^{2+}$ versus $\text{Na}^+/\text{Ca}^{2+}$ in water samples, shows lithologic units which affecting water quality. Based on the above diagram, the water chemistry is influenced by

silicate, evaporite and carbonate units, but the influence of silicate unit in water is more than of carbonate and sulfate units.

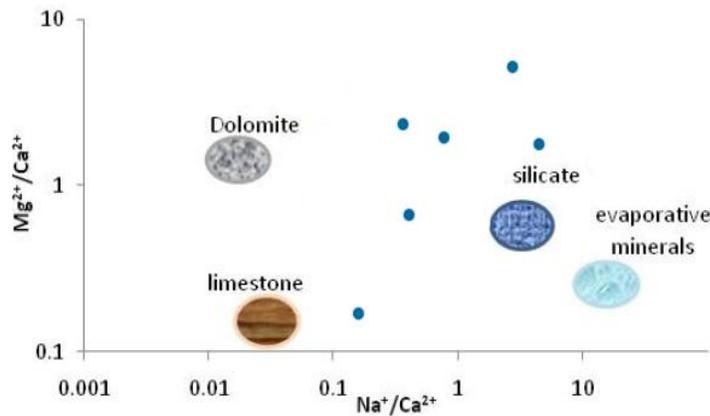


Fig. 5 Graph of logarithmic ratio of $\text{Na}^+/\text{Ca}^{2+}$ versus $\text{Mg}^{2+}/\text{Ca}^{2+}$

VI. FIELD PARAMETERS

pH: The normal pH range is from 6.5 to 8.5 [39]. The pH is one of the most important parameters concerning Cr mobility. The water samples of the Ophiolite springs and groundwaters are within a range of 7.9 to 9.1 with a mean 8.5 (Table II). Because Mg^{2+} and Ca^{2+} hydroxides are strong bases, their presence in the environment causes high pH alkaline water character [7]. In this study, only Al and Ca are found to be strongly correlated with pH.

TDS: TDS of waters ranges between 341-2929 ppm. TDS of some samples is within the maximum allowed limit, however the most of the sample are above the maximum permissible limit of WHO [39].

EC: The range of EC variation is 453 $\mu\text{s}/\text{cm}$ to 4650 $\mu\text{s}/\text{cm}$.

EC values in the up to 2000 $\mu\text{s}/\text{cm}$ is suitable for irrigation but most the amount of EC 1000 $\mu\text{s}/\text{cm}$ could be indicative of water pollution [39].

VII. ASSESSMENT OF WATER RESOURCES AND DRINKING WATER FACIES

The water samples in Rud Shur area exhibit a wide range of water qualities. All the waters are moderate alkaline (pH from 7.9 to 9.1). The waters show a wide range of major cation, anion and trace element concentrations. To show the chemical composition and hydrochemical facies of water resources, Piper diagram [25] Fig. 6 was used. They fit into five broad water types: 1) Mg-Cl 2) Mg- HCO_3 3) Na- HCO_3 4) Na-Cl and 5) Ca- SO_4 facies.

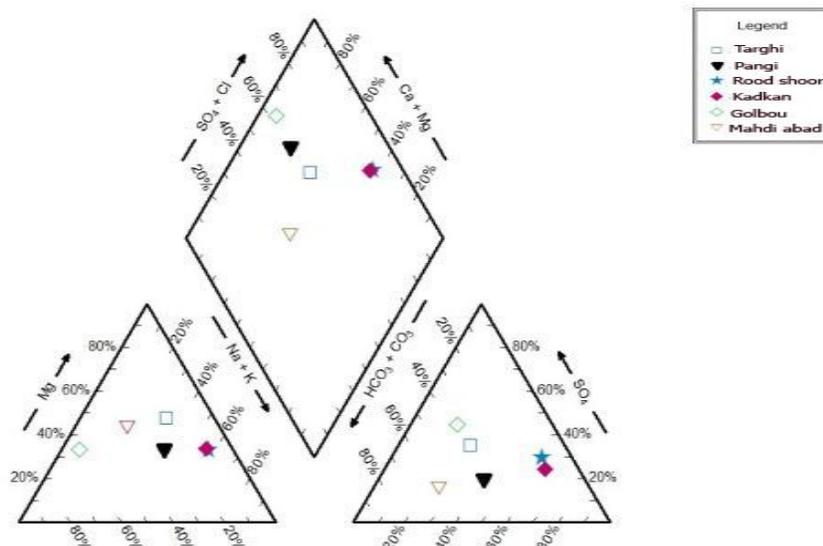


Fig. 6 Location of samples on Piper plot showing the relative proportions of major cations and anions for Pangli waters

To determine the feasibility of using water for drinking, Schuler charts [33] Fig. 7, and its indicators were used. On the basis of Schuler diagram, samples 1 and 6 good, No 5 as

acceptable sample but samples 2, 3 and 4 were not-potable. High amounts of Cl^- , Na^+ and Mg^{2+} in the samples are the main reason of unsuitability of waters for drinking.

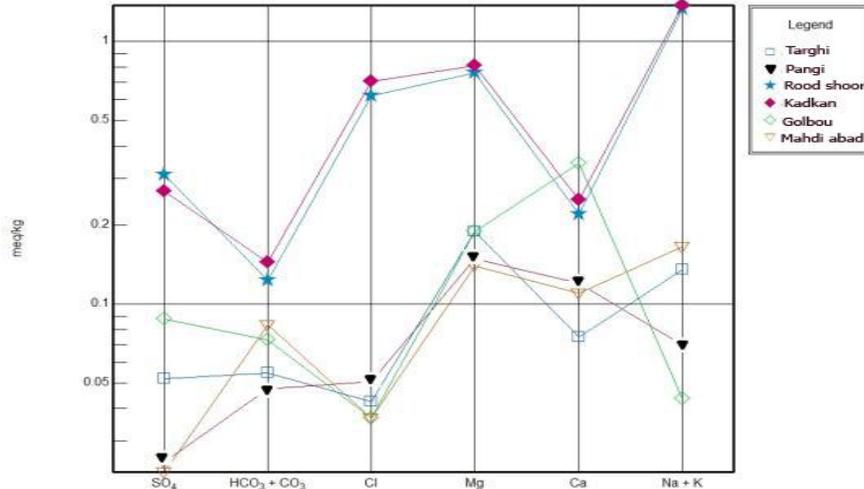


Fig. 7 Location of samples on Schuler diagram

In studies conducted in Italy and Mexico in most areas of ophiolitic area, the waters are Ca-HCO_3 and Mg-HCO_3 types [9]. They produce as a result of weathering of ultramafic rocks and serpentinite containing Cr(VI) and Cr(III) . Mg-HCO_3 water types, usually are produced through the interaction of meteoric water with serpentine and ultramafic rocks. Ca-HCO_3 water types are produced through interaction of meteoric water with gabbro and basalt rocks. Mg-HCO_3 water types are more rich in Cr than Ca-HCO_3 water types. One of samples was Mg-HCO_3 type and had the highest amounts of Cr in Pangli village (with a concentration of 97.4 ppb).

VIII. CONCLUSION

Hydrochemical variables of water resources in Pangli area were evaluated in order to enhance an understanding of the most significant processes which impact the hydrochemical variations. Major conclusions of this study are drawn as follows:

- As in the ophiolitic zone, pH is greater than neutral range ($\text{pH} > 7.9$) and $\text{DO} > 7.67 \text{ mg/l}$, Therefore, given the values of DO, Eh and alkaline pH of the water sample in the area, chromium in water resources area must contain significant amounts of Cr(VI) and is in the form of chromate (CrO_4^{2-}).
- The water chemistry of Pangli area is influenced by complex contamination sources and geochemical processes. In the area, rock-water interaction, carbonate mineral dissolution, silicate weathering and ion exchange reactions are the major hydrogeochemical processes responsible for contamination of water resources.
- Geochemical and hydrological processes controlling the concentration and speciation of chromium in water resources in the study area. The mean value of Cr cation (38.2 ppb) is higher than maximum permissible limit (ppb) in the waters of studied samples.

- An investigation of water resources associated with the ophiolite rocks of Pangli area shows five broad water types: 1) Mg-Cl 2) Mg-HCO_3 3) Na-HCO_3 4) Na-Cl , and 5) Ca-SO_4 facies.

- Important processes affecting the hydrochemistry of water resources as well as high amounts of Cl^- , Mg^{2+} , Ca^{2+} , HCO_3^- , TDS, EC and pH in waters are related to weathering of multicomponent spinel systems in ophiolitic complex. Therefore, oxidation of Cr(III) from Cr-spinels by high valent Fe and Mn oxides is main potential source of Cr(VI) contamination in serpentine soils and waters.

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