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Mineralogy of the Kraubath-type magnesite deposits of the Khuzdar area, Balochistan, Pakistan

Khuzdar Bölgesi (Belucistan, Pakistan)'ndeki Kraubath tipi manyezit yataklarının mineralojisi

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ABSTRACT

Mineralogical studies of the magnesite deposits in the Khuzdar District, Balochistan, Pakistan were made using the Xray diffraction (XRD) technique. These Kraubath-type magnesite deposits are hosted within serpentinized harzburgites, associated with Bela Ophiolite of Cretaceous age. The deposits occur as cryptocrystalline veins of stockwork-type, possessing botryoidal and bone habits. The ultramafic rocks of Bela Ophiolite were subjected to serpentinization. The hydrothermal fluids leached out Mg, Ca, Fe and other elements from the serpentinized rocks and finally carbonation of these ions resulted in the formation of their hydroxides and carbonates of different combinations to produce these deposits. The XRD analysis of the ores revealed a high magnesite content in association with artinite, brucite, huntite, Femagnesite, dolomite, calcite and Mg-calcite. Initially, at low temperatures and low partial pressure from carbon dioxide (PCO_2), metastable hydroxides and carbonates are formed, and these are gradually converted into a stable magnesite phase. The low abundance of allied minerals reflects the relatively high temperature conditions and PCO_2 that convert metastable minerals into their stable magnesite phase. The study revealed an increasing temperature and PCO_2 from brucite through artinite, hydromagnesite, huntite, and dolomite to magnesite. Principal component analysis (PCA) and correlation matrix analysis were also utilized to reveal the genetic affiliation that existed between these minerals.

Keywords: Balochistan, Khuzdar, Kraubath-type magnesite, mineralogy, Pakistan.

ÖΖ

Khuzdar Bölgesi (Belucistan, Pakistan)'ndeki manyezit yataklarının mineralojisi X-ışınları kırınım tekniğiyle araştırılmıştır. Kraubath tipi bu manyezit yatakları, Kretase yaşlı Bela ofiyolitleriyle ilişkili serpantinleşmiş harzburjitler içinde yer almaktadır. Bu çökeller, kriptokristalin damarlar ve botriyodal ve kemiksi. özelliklere sahip ağsı yatak şeklinde oluşmuşlardır. Bela ofiyolitik kayaçları serpantinleşmeye maruz kalmışlardır. Hidrotermal akışkanlarca taşınan Mg, Ca, Fe ve serpantinleşmiş kayalardan gelen diğer elementler ve sonuçta bu iyonların karbonatlaşması, bunların hidroksitlerinin oluşumuyla ve farklı bileşimlerdeki karbonatların bu çökelleri oluşturmasıyla sonuçlanmıştır. Cevherlerin X-ışınları kırınım analizleri; artinit, brusit, huntit, Fe-manyezit, dolomit, kalsit ve Mg-kalistle ilişkili yüksek manyezit içeriğinin varlığını göstermektedir. İlk olarak, düşük sıcaklıkta ve düşük kısmi karbondioksit (PCO₂) basıncı altında, tedricen duraylı manyezit fazına dönüşen yarı-duraylı hidroksitler ve karbonatlar oluşmuştur. Yabancı minerallerin azlığı, göreceli olarak yüksek sıcaklık koşullarına ve yarı-duraylı mineralleri manyezit fazına dönüştüren PCO₂'ye işaret etmektedir. Bu çalışma, artan sıcaklığı ve arinit, hidromanyezit, huntit, dolomitten itibaren brusitten PCO₂ artışını göstermiştir. Ayrıca asal bileşen analizi (PCA) ve korelasyon matriksi analizi bu mineraller arasında mevcut olan kökensel ilişknin araştırılmasıi için kullanılmıştır.

Anahtar Kelimeler: Belucistan, Khuzdar, Kraubath tipi manyezit, mineraloji, Pakistan.

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INTRODUCTION

Regionally, the study area belongs to the ophiolite thrust belt, which marks the boundary between the Indian and Eurasian plates. Along the ophiolite, sedimentary rocks of Jurassic to Tertiary age are also exposed on either side (Figure 1). The Bela Ophiolite is linked with the Alpine-Himalayan Mesozoic Belt, which stretches from the European Alps to the Himalayas. The Bela Ophiolite has characteristics of both a suprasubduction zone and mid-ocean ridge settings, and is also intruded by hotspot-derived magmas (Khan et al., 2007). Sheth (2008) also verified the above assumption and showed occurrences of rocks with affinities to Mid Oceanic Ridge Basalt (MORB), Ocean Island Basalt (OIB) and Island Arc Basalt (IAB) in the Bela Ophiolite.

Magnesite deposits are formed by a number of processes (Pohl and Siegl, 1986; Schroll, 2002). Among them two genetic types are important, and the first type is known as the Veitsch type. These are replacement-type and strata-bound lensoid deposits, consisting of coarse crystalline spar-magnesite hosted by marine platform sediments. The second type of deposit is cryptocrystalline and known as the Kraubath type. These deposits are much smaller and less frequent than the Veitsch-type. Bashir (2008) revealed that the magnesites of the study area are genetically affiliated with cryptocrystalline Kraubath type magnesite. They are commonly found in contact with or in close proximity to the serpentinized ultramafic rocks of the Alpine ophiolites (Sasvári and Kondela, 2007; Gartzos, 2004).

The obduction of the Bela Ophiolite over the continental margin of the Indian Plate creates a number of fractures and cracks in the host rock. The fracturing phenomenon facilitates water to initiate hydration of the ferromagnesian rocks, causing serpentinization. The serpentinized rocks release Mg, Ca, Fe etc. via dissolution, leaching or other mineral-alteration reactions. The released Mg ions may react with water molecules to form brucite. Subsequently, Mg along with Ca and Fe can react with dissolved CO_2 to precipitate different carbonate

minerals. The CO_2 -rich fluids were either derived from decarbonation of deep-seated carbonates or decarboxylation of organic rich sediments (Gartzos, 2004; Zedef et al., 2000).

Showings and deposits of Kraubath-type cryptocrystalline magnesite are widely exposed within the Bela Ophiolite of the Cretaceous age. These deposits are hosted within the upper part of highly fractured and imbricated ultramafic complexes containing the serpentinized equivalent of harzburgite (Bashir, 2008). The promising deposits are in Baran Lak, Pahar Khan, Gangu and Nal (see Figure 1), and are being mined locally (Bashir et al., 2004). Magnesite occurs either as veins, stockwork or as irregular masses posessing botryoidal and bone habits.

Various carbonates and hydroxides of Mg occur in the study area with varying proportions in different localities. Each Mg-mineral exhibits a typical regime of formation and stability under varying temperature, water and carbon dioxide partial pressure (PCO₂). The mineralogical convergence and the occurrence of the magnesite minerals appear to be tools to illustrate the dominance of kinetic and physicochemical processes that prevailed in the study area during the formation of these minerals. The potential for decomposition of metastable hydrated magnesium carbonate phases to stable magnesite may represent the long-term stability of the products of mineral sequestration (Wilson et al., 2009). The obduction of ophiolite, tectonics pulses and emplacement of dykes also contribute to variation in the geochemical environment.

The aim of this paper is to present the results of a study of the mineralogy of the magnesite deposits of the Khuzdar area, in order to infer from these the impact of kinetic and physicochemical processes on the genesis of magnesite and allied minerals. The present study also highlighted the transformation pathway of magnesite through the process of serpentinization. The mineralogical information obtained from this study may assists miners, exploiters and industrialists in better utilizing magnesite ore in Pakistan so that the mineral sector can play its proper role in boosting the economy of that country.



Figure 1. Simplified map of the Khuzdar area showing sampling sites. Şekil 1. Örnekleme noktalarını gösteren Khuzdar bölgesinin yalınlaştırılmış haritası.

ANALYTICAL METHODS

The samples of host rocks and magnesites were first crushed using a jaw crusher, and ground in a tema mill. The pulverized (-200 mesh) and moisture free samples were used for X-ray analysis. The analyses of magnesite samples were carried out using a Bruker AXS 5000 X-ray diffractometer. Cu and K α radiation was used during the analysis. The diffractometer was operated at 40 KV and 30 Ma. Randomly oriented amounts of the samples were scanned from 10°-90° (2 θ) with a step size of 0.05° (2 θ). The scanning speed was one degree per second.

RESULTS AND DISCUSSIONS

Brucite

Brucite $[Mg (OH)_2]$ is reported from four samples (UW2, PS, CG and SB) was studied through X-ray diffractograms. It shows a wide range of concentration (2-12.7%). The brucite shows association with other Mg bearing minerals but more commonly it is related to magnesite and, to a lesser degree, with calcite (Table 1). Probably in the initial phase, the Mg ions released from serpentinites are surrounded by

water molecules forming brucite (Figure 2). Kinetically, brucites are formed at a low temperature, a basic pH and at a low PCO_2 .

Brucite [Mg (OH)₂] deposits of economic interest are genetically linked to shallow level igneous rocks intruded into dolomite and/or magnesitebearing sedimentary or metasedimentary rocks (Simandl et al., 2007). Brucite is widely distributed in ultramafic rocks (Hora, 1998). The fibrous variety of brucite is common in ultramafic rocks, where it coexists with chrysotile (Ross and No-

Table 1. Mineral contents (%) of selected ore samples acquired by XRD analysis. *Çizelge 1. Cevher örneklerinin X-ışınları kırınım analiziyle belirlenmiş mineral içerikleri (%).*

Sample No.	Magnesite	Fe- magnesite	Calcite	Mg- calcite	Dolomite	Artinite	Huntite	Brucite	Periclase	Aragonite	Hydro- magnesite	Borcarite
BB2					7						93	
LN3	72.6				4.1	23.3						
LK3	49.6		2.8				3			44.6		
KK4	89			7.7	3.47							
GG7		97.8	1.4		0.8							
UE2	98.6		1.4									
UE9	61.3				4.4	34.4						
UW1	97.4		2.6									
UW5	70.5		1.8	1.6	1.7		1.74	9.6	10.7			
AT5	95		3.1		1.9							
KC4	88		9.7		2.3							
KW2	43.2		18.4		4.2	34.2						
KW3	37.3		0.8		38.8	23						
KE3	88.2			8.5	3.4							
PK5	93.4		3.7				2.9					
CM2		94	5.1		0.9							
PS4	95.4		2.7					2				
CG1	77.5		9.8					12.7				
BN4	96		1.3		2.7							
BN8		99.1	0.5		0.4							
BE2	94.2		3.7		2.1							
BE6			94.2		1.4		4.3					
BL4			70.5		8.3	21.2						
BS4	94.1		1.8	2.5	1.6							
BS7	89.6			8.6	1.8							
SG4	53.7		1.5	2	1.8	31.9	9.1					
GD3	83.8		10		6.2							
SN3		76.1		1.8		18						4.2
SB1	5		92.9					2				



Figure 2. Schematic representation of model of magnesite formation at Khuzdar region. Şekil 2. Khuzdar bölgesindeki manyezit oluşum modelinin şematik gösterimi.

lan, 2003). In most contact metamorphic settings, periclase does not survive the retrograde metamorphism that follows a metamorphic climax and it rehydrates to form brucite which, in turn, readily alters to hydromagnesite. If the water fraction is extremely high, brucite may form directly by magnesites or dolomites. Brucite can also be formed through the decomposition of magnesian minerals without carbonation during the weathering of serpentine. The widespread occurrence of brucite in Alpine serpentinites implies that pressure temperature conditions during serpentinization were commonly in the range of 400°C and 1.034 kbars of water vapor pressure.

The reaction of brucite with CO₂-bearing groundwater at depth is probably responsible for much of the magnesite associated with serpentinites. Ultramafic-hosted deposits have been considered as potential sources of brucite (Liu et al., 2004). In the presence of water, brucite is a thermodynamically stable solid, until the PCO_2 reaches $10^{-6.3}$ bar, above which anhydrous MgCO₃ (magnesite) becomes stable (Lippmann, 1973), through various steps (see Figure 2).

Artinite

Artinite [Mg₂(CO₂)(OH)₂.3H₂O] is a less abundant mineral in the studied samples (see Table 1). It is noteworthy that its presence is mostly confined to those samples that had contact with the host rocks. Most probably the artinites were formed by groundwater action on existing magnesite. In the rotated space diagram (Figure 3) both artinite and dolomite are plotted close to each other, indicating genetic affiliation. The above assumptions are also supported by the negative correlation of artinite with other minerals, except huntite which shows a slight positive correlation (Table 2). It is assumed by many researchers that the transformation of artinite through other minerals is a recent phenomenon.

Artinite belongs to the monoclinic group that may form under high PCO_2 (Frost et al., 2008). It is a low temperature mineral usually found in weathered or altered ultramafic rocks, typically serpentinites. It commonly associates with brucite, hydromagnesite, aragonite, dolomite and magnesite. In a hydrous and near surface oxidation environment, brucite may convert into artinite. It is most likely that smaller PO_2 values



Figure 3. Rotated space diagram (PCA) showing the genetic affiliation of different ore minerals determined through XRD analysis.

are required for conversion of brucite to artinite (Horstetler et al., 1996).

Hydromagnesite

Hydromagnesite $[Mg_5(CO_3)_4(OH)_2 \cdot 4(H_2O)]$ was found only in sample BB (see Table 1), which belongs to the northern extremity of the study area where highly disturbed exotic blocks of ophiolite are present. The sample BB has hydromagnesite (93%) as its predominant mineralogy, along-with dolomite (7%). The existence of these two minerals in the BB locality is a little strange, although their genetic affiliation exists in nature. It is speculated that the high tectonism of the area will favour the formation of magnesite; later, during exposure and in near

 Table 2. Correlation matrix of the mineralogical data of selected samples.

 Cizelae 2. Secilmis örneklere ait mineralojik verinin korelasyon matrisi

	Fe- magnesite	Calcite	Mg- calcite	Dolomite	Artinite	Huntite	Brucite	Periclase	Aragonite	Hydro- magnesite
Magnesite	-0.59	-0.47	0.31	-0.13	-0.23	-0.09	0.10	0.06	-0.04	-0.28
Fe- magnesite Calcite		-0.15	-0.14	-0.16	-0.08	-0.14	-0.12	-0.07	-0.07	-0.07
			-0.21	-0.04	0.01	0.14	0.02	-0.07	-0.06	-0.08
Mg-calcite				-0.05	-0.16	-0.05	-0.09	0.01	-0.09	-0.09
Dolomite					0.36	-0.12	-0.13	-0.05	-0.09	0.10
Artinite						0.24	-0.17	-0.10	-0.10	-0.10
Huntite							-0.01	0.10	0.23	-0.07
Brucite								0.57	-0.06	-0.06
Periclase									-0.03	-0.03
Aragonite										-0.03

Şekil 3. X-ışınları kırınım analiziyle belirlenmiş olan farklı cevher minerallerinin kökensel ilişkisini gösteren döndürülmüş konum diyagramı (PCA).

surface conditions, the magnesites of the area were hydrated to hydromagnesites. Calcium may have been introduced through groundwater, forming minor dolomite, but this conversion is not simple and requires multiple steps under the influence of local tectonics. Therefore, PCA (see Figure 3) analysis explicates no genetic affiliation between the two minerals. This statement is also strengthened by the weak correlation matrix (0.096).

Hydromagnesite occurs generally as encrustations and fracture fillings in altered ultramafic rocks and serpentinites, and in low temperature, hydrothermally altered dolomitic xenoliths and marble; it is also found as concretions and in massive form. At low-temperatures, instead of magnesite, hydromagnesite is common (Deelman, 2003). The brucite is destabilized in surface environments, and depending on the degree of weathering and ore type, it may be converted into hydromagnesite. Brucite is converted to hydromagnesite if the PCO₂ is at least 10⁻⁶ bar (Horstetler et al., 1996). The alteration of brucite into hydromagnesite or artinite is restricted to the top 5m. Hydromagnesite undergoes an endothermic decomposition with H₂O and CO₂ releases in the temperature range of 200-550°C. Haurie et al. (2007) investigated the thermal behaviour of hydromagnesite under the influence of heating rate, sample size and environmental conditions. Hydromagnesite releases lattice water in the temperature range of 200-325°C, the dehydroxylation occurs in the range of 375-450°C and the decarbonation from 500 to 550°C (Sawada et al., 1979; Khan et al., 2001).

Dolomite

Dolomite [(CaMg)CO₃] is found as the second most abundant mineral in the studied samples (see Table 1), with low concentrations (7-0.4%). From the distribution of Mg-bearing minerals in the study area it can be understood that the carbonation of brucite leads to the formation of artinite which, upon strong carbonation, is converted into stable carbonates. However, in the presence of Ca ions dolomite is formed. Possibly, either groundwater or the chemistry of the host rock is responsible for the contribution of Ca in the area. The moderate correlation matrix of dolomite with artinite (see Table 2) further supports the prevalence of minerals formed according to the above hypothesis, in the area. The PCA also reveals a close association between dolomite and artinite (see Figure 3). The sample KW2 has an exceptionally high dolomite content of (38.8%), demonstrating the impact of the host rock. In the Khushal (west) locality, the associated host rock contains a relatively higher proportion of Ca (20.03%). Probably, the formation of dolomite is controlled by the initial Ca/Mg ratio of the host rock and also by other kinetic factors.

Huntite

Huntite $[Mg_{3}Ca(CO_{3})_{4}]$ is reported from five samples of the study area (see Table 1). The abundance of huntite ranges from 9.1-1.74% with a mean of 4.21%. The concentration decreases from the south to the north of the study area. The huntite shows a moderate correlation with dolomite and aragonite (see Table 2). It is interesting that in the sample LK, where aragonite is reported, the dolomite is not determined, and this may be due to thermodynamic factors. The study area indicates that huntite is precipitated earlier than dolomite.

Huntite crystallizes in a trigonal system and its structure is similar to that of dolomite. Huntite formations include different types of minerals such as hydromagnesite, magnesite, aragonite and dolomite (Kangal and Güney, 2006). Huntite can form at low temperature surface or near-surface conditions; either by direct precipitation from Mg-rich solutions or by interaction of Mg-rich water with precursor carbonates minerals (Dollase and Reeder, 1986). It also occurred as a coating in fissures of the weathered serpentinite immediately below the soil profile. Davies et al. (1977) have experimentally shown that huntite always precipitates before dolomite, depending upon an increase in CO22-concentration. Huntite grows before dolomite because its more open structure allows enhanced Mg dehydration (Lippmann, 1973).

Magnesite

Magnesite (MgCO₃) is the major mineral of the Kraubath type of deposits. It commonly origina-

tes from the alteration of Mg-rich rocks during low grade metamorphism while they are in contact with carbonate-rich solutions. Magnesite occurs as veins in, and as an alteration product of, ultramafic rocks of ophiolite affinity, serpentine and other Mg-rich rock types in both contact and regional metamorphic terrain.

According to XRD analysis, mangesite is the most dominant and widely occurring carbonate mineral in the study area (see Table 1). Magnesite exhibits a negative correlation matrix with most of the minerals except brucite and periclase (see Table 2). It is formed at the expense of these minerals (Figure 4). Magnesite is the stable phase among the Mg-hydroxides and carbonate, and it is the end product of all such phases (see Figure 2). Yalçın and Bozkaya (2004) point out the alteration trend of host and ore minerals on a triangular diagram (SiO₂-CaO-MgO). The plots of the host rocks and ores (Figure 5) clearly demonstrate that the magnesite and talc of the study area were generated through the carbonation of serpentine (Eq. 1) to brucite, magnesite, dolomite and calcite.

$$2Mg_{3}Si_{2}O_{5}(OH)_{4} + 3CO_{2} \rightarrow Mg_{3}Si_{4}O_{10}(OH)_{2}$$
$$+ 3MgCO_{3} + 3H_{2}O$$
(1)

Further carbonation of talc converts into magnesite (Eq. 2).

$$Mg_{3}Si_{4}O_{10}(OH)_{2} + 3CO_{2} \rightarrow 3MgCO_{3} + 4SiO_{2}$$
$$+ H_{2}O$$
(2)

Ferroan magnesite is present in samples SN (76.1%), BN2 (99.1%), GG (97.8%) and CM (94.0%). In these localities, Fe may be capable of entering into the magnesite, most probably at elevated temperatures. The genetic affiliation of magnesite is also supplemented by PCA, which shows a close association between the hydroxides and carbonates of Mg in the study area (see Figure 3).

Simandl et al. (2001) and Papenguth et al. (2000) depict a triangular variation diagram (MgO-CO₂-H₂O) to illustrate the mineralogical fields of



Figure 4. Bivariate plot showing the relationship between magnesite and other minerals.





- Figure 5. Composition of ultramafic rocks of the study area and their alteration products on the SiO₂-CaO-MgO diagram (after Yalçın and Bozkaya, 2004).
- Şekil 5. Çalışma alanındaki ultramafik kayaçların bileşiminin ve bunların alterasyon ürünlerinin SiO₂-CaO-MgO diyagramında gösterimi (Yalçın ve Bozkaya, 2004'ten).



- Figure 6. Ternary plot MgO-CO₂-H₂O (Mole %) showing mineralogical composition of magnesites of study area (Mineralogical fields after Simandl et al., 2001 and Papenguth et al., 2000).
- Şekil 6. Çalışma alanındaki manyezitlerin mineralojik bileşimini gösteren MgO-CO₂-H₂O (Mol %) üçgen diyagramı (Mineralojik alanlar Simandl vd., 2001 ve Papenguth vd., 2000'den)

the Mg-mineral array. The samples of magnesite from the study area on the MgO-CO₂-H₂O diagram (Figure 6) exhibit a schematic reaction path from hydromagnesite to magnesite. The hydration-and-carbonation reaction path in the MgO-CO₂-H₂O system at ambient temperature and atmospheric CO₂ provides us with a better understanding of the low temperature alteration ultramafic rocks, and consequently the convergence of various Mg-minerals. The reaction path involving carbonation of brucite (Mg(OH))) is particularly complex, as Mg has a strong tendency to form a series of metastable hydrous carbonates. These metastable hydrous carbonates include hydromagnesite, artinite and nesquehonite. Water also plays an important role in the formation of hydrated MgCO₃ minerals. Where there is a higher availability of H₂O and CO₂, nesquehonite will form, and at low PCO₂ (10-2 bar) it alters to hydromagnesite (Stamatakis, 1995; Canterford et al., 1984) through a proto-hydromagnesite intermediary. Botha and Strydom (2001) also verify the presence of an intermediate phase between nesquehonite and hydromagnesite, which shows similarities with hydromagnesite. Möller (1989) experimentally verified that magnesite precipitation proceeds via hydromagnesite at elevated T.

Periclase

Periclase (MgO) is a comparatively uncommon mineral in the Kraubath-type magnesite deposits. It is a relatively high temperature mineral, formed from the high grade metamorphism of dolomites along with calcite and carbon dioxide. Upon weathering, periclase easily alters to brucite/hydromagnesite.

Periclase is found only in sample UW2 in association with brucite (see Table 1) and with small amounts of dolomite, calcite and huntite. The alliance of periclase and brucite is proved by correlation matrix (0.575). Both minerals possess the strongest correlation of all other minerals. The rotated space diagram also signifies a very close association of brucite with periclase (see Figure 3). The presence of all three phases—magnesite, brucite and periclase—in the sample UW2 reflects an increase in temperature along with CO_2 in fluid during prograde metamorphism, as mentioned by Miyashiro (1994). The high temperature causing different grades of metamorphism may be due to the emplacement of dikes. The high temperature metamorphism can also be witnessed bythe adjacent host rock, which is intensively altered with numerous veins. Brucite decomposes into periclase and H₂O at 3.6 GPa and 1050°C, while no periclase is formed after the decomposition of brucite at 6.2 GPa and 1150°C, indicating that the solubility of the MgO component in H₂O greatly increases with increasing pressure (Okada et al., 2002).

Calcite

Calcite (CaCO₃) is present as a minor constituent in nearly all samples from the study area except for a few where it appears as major mineral (see Table 1). The low abundance of calcite in the area perhaps indicates Ca-poor ultramafic rock disassociation in the initial phase. The high Mg-bearing water would also inhibit the growth of calcite. Calcitization of magnesite occurred through the interaction of magnesite and Ca-enriched waters derived from the dissolution of Ca-bearing rocks under near-surface conditions in the later phase, as has also been observed by Canaveras et al. (1998). The fine sized magnesite promotes the alteration into calcite. Lacin et al. (2005) and Demir and Dönmez (2008) have demonstrated that the dissolution rate of magnesite increases with decreasing particle size and with increasing temperature. It is also possible that the conversion of calcite occurs from dolomite rather than from magnesite, because the dissolution rate of dolomite is much faster than that of magnesite (Chen and Tao, 2004).

In a few locations around Baran Lak (Sample BE2 and BL), calcite appears as the chief constituent (see Table 1). Magnesite is absent and the dolomite, huntite and artinite are associated minor minerals. The association indicates that the calcite was formed through the artinite to huntite and dolomite. At higher PCO₂, dolomite and huntite are formed, depending on the physicochemical conditions. These are unstable and gradually convert to low Mg-calcites.

Aragonite

Aragonite $(CaCO_3)$ is a polymorph of calcite. It does not occur commonly in the study area. It is possible that, in the Mg-rich water, calcite precipitation was inhibited by adsorption of Mg to the surface of incipient crystals, so aragonite precipitated instead; it later altered to the more stable calcite.

In the study area, it is only found in the Lukh locality. The sample LK contains 44.6% aragonite along with 49.6% magnesite. This implies that the magnesite of the area suffered calcification which removes Mg, and as a result aragonite is formed. The area is an enclave within the vast exposure of Nal Limestone of the Late Oligocene-Early Miocene age. Ca was probably introduced in the magnesite from the dissolution of Nal limestone. In general, the crystallization of aragonite is favoured by temperatures of 50-80°C and requires more pressure than calcite (Deer et al., 1992). It is metastable at room temperature-pressure and alters to calcite with the passage of time. This indicates that aragonite is formed by an epigenetic process at the expense of magnesite. Furthermore, aragonite enables the inclusion of Mg ions in its structure because of the ionic difference between Ca (1.18Å) and Mg (0.72Å). A maximum of just 1 mole% MgCO₃ can exist in aragonite, even up to 800°C; Mg does not enter significantly in aragonite structure. Magnesium is also less soluble in aragonitic structure than in calcite.

CONCLUSIONS

The Kraubath-type magnesite deposits are widely present in the Khuzdar District of Balochistan, Pakistan. The magnesite deposits of the study area possess a cryptocrystalline nature, a botryoidal/bone habit and are found as thick veins and stockwork in ultramafic rocks. These magnesite deposits are confined to the ultramafic segment of the Bela Ophiolite of Cretaceous age. The host rocks are mostly serpentinized harzburgite, formed during intense alteration and low grade metamorphism.

The obduction of Bela Ophiolite over the continental margin of the Indian Plate creates a number of fractures and cracks in the host rock. The fracturing phenomenon facilitates water to initiate hydration of the ferromagnesian rocks, causing serpentinization. Magnesite was deposited in progressively opening fractures as CO_2 was lost from the solutions when they approached the surface. The plots of the host rocks and magnesites on a SiO₂-CaO-MgO diagram showed that the magnesite of the study area was generated through the alteration of serpentine and talc.

Brucite is the first mineral formed through hydration of Mg ions. It is only stable at low temperatures, a basic pH and at a low PCO₂. At higher partial pressure CO₂ it will transform into either hydromagnesite or artinite. At elevated temperatures, hydromagnesite gradually converts into magnesite. Calcium in the system may contribute through host rocks or may be supplied through meteoric water. In the presence of Ca ions, huntite starts to crystallize, and this happens with lower concentrations of carbonate ions than are required for dolomite. At elevated concentrations of carbonate ions, huntite is converted into dolomite, which is more stable. Magnesite is the most dominant and widely occurring carbonate mineral in the study area. The existence of a low abundance of allied minerals (dolomite, artinite, brucite, huntite and Fe-magnesite) indicates their initial formations as hydroxides and carbonates. These metastable minerals can convert finally into magnesite over time. The conversion is mainly controlled by the temperature, PCO, and level of water saturation. The trend shows increasing temperatures and PCO₂ from brucite, artinite, hydromagnesite, huntitite, dolomite to magnesite.

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