MINERALOGY, GEOCHEMISTRY AND ORIGIN OF CRETACEOUS CHERT FROM WADI AL-WALA, CENTRAL JORDAN

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ABSTRACT

This research is aimed at detailed investigation of the origin chert rocks in Wadi Al-Wala area in central Jordan. The chert in the area is of Upper Cretaceous in age and belongs to the widely distributed chert on the western margin of the Arabian Plate. Field characteristic structures of these cherts indicate that they occur in three forms: bedded, concretion and brecciated structure. Nine representative samples were selected for the present study.

The mineralogical study shows that the chert is mainly consisted of microcrystalline quartz, calcite microcrystalline quartz, fossils and phosphatic microcrystalline quartz. The bedded chert are composed almost entirely of microcrystalline quartz and secreting organism. Geochemical investigation of Wadi Al-Wala chert shows that the content of trace elements is considerably variable, and most trace elements are low. This may indicate that the chert in the study area is resulted from the leaching of country rocks by hydrothermal solution and the evidence from submarine hydrothermal origin of silica forming this chert. This is further supported by the low MnO/Fe\textsubscript{2}O\textsubscript{3} ratio, Cr/Zn and Ni/Zn ratios.

Keywords: Chert; Wadi Al-Wala; Geochemistry; Mineralogy; Replacement

INTRODUCTION

The Upper Cretaceous chert in central Jordan has been divided into three types, bedded, brecciated and concretion types which occur in an alternating manner with limestone or scattered throughout the sequence. The banded chert is devoid of any organic structure. The brecciated chert has angular chert fragment that set in a matrix of
cryptocrystalline quartz and shows slightly different colors. The concretion chert retains the organic structure of limestone. Stratigraphy of the Upper Cretaceous sediment in central Jordan has been studied by Burdon (1959); Bender (1968 and 1974); Mohammad and Al-Fugha (1991); Mohammad (1992); Al-Malabeh (1994); Masri (2003) and Al-Malabeh et al. (2017). The stratigraphic section concerning the chert of this unit were studied and sampled at Wadi Al-Wala in central Jordan (Fig. 1). The history of solidification and the replacement or dissolution of siliceous bioclasts is protracted, ranging from near the sediment certification occurred by a combination of force of crystallization controlled replacement of host carbonate. Differences in sediment porosity and biogenic silica concentration promote the nucleation of chert concretion in some formation. The concretion chert forms by the replacement of carbonate rock or sediment, which are formed primarily by replacement of limestone as opposed to bedded chert which is formed primarily by recrystallization of siliceous oozes (Robert et al., 1989; Al-Malabeh and Kempe, 2005). Bedding planes within the Wala formation contain abundant black chert and in the concretion are found to be very fossiliferous. The chert concretion and the surrounding carbonate were studied in order to interpret silica sources previous studies suggest the concretion formed exclusively from biogenic silica. Another study would suggest and an additional source of silica is the volcanism associated with tectonic orogeny (Rice, 2004; Al-Malabeh and Kempe, 2012). In the study area, two basaltic flows intercalated with pyroclastic rocks of Pleistocene age where observed.

The aim of the present study is to describe the mineralogical, geochemical and origin of chert in Wadi Al-Wala, central Jordan (Fig. 1). It is important to stress out that the origin of silica and the mechanism that lead to the formation of cherts are poorly understood in this area.
Fig. 1: Location map of the study area, Wadi Al-Wala, central Jordan

Geologic Setting
The southwest of Jordan forms a part of the Precambrian Arabian-Nubian Shield (ANS), whereas the rest of the country is covered by the Phanerozoic rocks. Cretaceous carbonates rocks are the most dominant and oldest rock group outcrop in the study area. The chert in central Jordan belongs to Upper Cretaceous member of Arnman silicified limestone formation is of Santomia age (Mohammad, 1992). The formation consists of a dark grayish thick bedded brecciated chert, grayish microcrystalline limestone and dolomitic chalky marl and phosphatic rocks. The chert occurs bedded, brecciated and
concretion forms are three morphologies present in the study section. The chert make about 30% of the constitute of the stratigraphic section where the color of the chert ranges from nearly light brown to black and dark gray being most common. Bedded and concretions chert are the main forms occurs in an alternating manner with limestone while the brecciated chert are loss common forms occurs in random distribution or parallel to the bedding planes. In some cherts amount of a demised carbonate occur. The chert concretions range in diameters from 5 to 20 cm where the brecciated cherts range from 35 – 85 cm. The bedded cherts range in thickness from ten cm up to 1.5 m sometimes these beds attain two meters thick alternating with 3 to 4 meters limestone beds. The structure of Wadi Al-Wala controlled by a major fault trending E-W and its generally affected by a series of small anticlines and synclines. The fold axis extensions from ten cm up to tens of meters Wadi Al-Wala is enclosed with complex dome structure with axis direction related to the adjacent fault. The general geology of Wadi Al-Wala was studied by Bender (1968 and 1974); Mohammad (1992); Masri (2003) and Al-Fugha and Tharwat (2010).

The Late Cretaceous Amman formation in central Jordan, the microfacies indicate a deposition with a shallow marine inner epicontiental shelf environment. The section concerning the chert of this unit were studied and sampled at Wadi Al-Wala in central Jordan. This section is consists of limestone with chert where the sequence attains 70 m thick in Wadi Al-Wala.

**Methods and Techniques**

The field study was carried out to classify upper cretaceous chert in central Jordan into three stratigraphic types bedded, brecciated and concretion forms. The petrographic and mineralogical of the samples were studied under the polarizing microscope. Chemical analyses have been analyzed for major and trace elements content by using X-Ray fluorescence (XRF) the data are presented in Table (1).
Table 1: Chemical analysis of whole chert samples from Wadi Al-Wala central Jordan, major oxides in wt % and trace elements concentrations in ppm

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Asl 1</th>
<th>Asl 2</th>
<th>Asl 3</th>
<th>Asl 4</th>
<th>Asl 5</th>
<th>Asl 6</th>
<th>Asl 7</th>
<th>Asl 8</th>
<th>Asl 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>93.54</td>
<td>61.18</td>
<td>97.3</td>
<td>93.75</td>
<td>81.47</td>
<td>69.65</td>
<td>96.93</td>
<td>95.7</td>
<td>92.47</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.16</td>
<td>0.00</td>
<td>0.12</td>
<td>0.12</td>
<td>0.0</td>
<td>0.0</td>
<td>0.18</td>
<td>0.65</td>
<td>0.13</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.07</td>
<td>0.02</td>
<td>00.00</td>
<td>0.0</td>
<td>0.06</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.3</td>
<td>0.0</td>
<td>0.01</td>
<td>0.25</td>
<td>0.23</td>
<td>0.05</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>CaO</td>
<td>3.04</td>
<td>22.67</td>
<td>0.65</td>
<td>3.74</td>
<td>3.65</td>
<td>17.95</td>
<td>0.87</td>
<td>1.08</td>
<td>3.09</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
<td>0.00</td>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.2</td>
<td>0.2</td>
<td>0.04</td>
<td>0.17</td>
<td>0.15</td>
<td>0.42</td>
<td>0.1</td>
<td>0.36</td>
<td>0.57</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.44</td>
<td>0.68</td>
<td>0.92</td>
<td>0.95</td>
<td>0.97</td>
<td>1.67</td>
<td>0.85</td>
<td>1.53</td>
<td>0.93</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.1</td>
<td>15.5</td>
<td>2.93</td>
<td>5.9</td>
<td>13.6</td>
<td>10.22</td>
<td>6.2</td>
<td>0.75</td>
<td>1.65</td>
</tr>
<tr>
<td>Total</td>
<td>99.6</td>
<td>100.6</td>
<td>100.38</td>
<td>99.38</td>
<td>100.1</td>
<td>100.01</td>
<td>99.69</td>
<td>98.3</td>
<td>99.03</td>
</tr>
</tbody>
</table>

Trace elements in ppm

| V    | 14.08 | 3.15  | 15.05 | 14.78 | 7.15  | 5.12  | 16.08 | 14.95 | 14.02 |
| Cr   | 37.92 | 70.57 | 35.64 | 35.72 | 60.42 | 61.06 | 39.42 | 35.27 | 37.65 |
| Ni   | 0.0   | 9.06  | 0.0   | 0.0   | 6.07  | 7.15  | 0.0   | 0.0   | 0.0   |
| Zn   | 44.69 | 303.5 | 46.5  | 42.2  | 286   | 287.85| 35.26 | 45.62 | 42.65 |
| As   | 3.76  | 3.9   | 3.45  | 3.2   | 3.45  | 3.82  | 3.42  | 3.27  | 3.72  |
| Se   | 1.03  | 1.26  | 1.01  | 1.05  | 1.15  | 1.15  | 1.37  | 1.02  | 1.07  |
| Ta   | 1.89  | 0.2   | 1.72  | 1.72  | 0.74  | 0.35  | 0.95  | 1.63  | 1.92  |
| W    | 3.11  | 1.9   | 3.96  | 3.15  | 2.17  | 1.75  | 3.85  | 3.72  | 3.25  |
| Pb   | 2.72  | 1.68  | 2.84  | 2.6   | 2.23  | 1.92  | 2.74  | 2.58  | 2.56  |
| Bi   | 1.83  | 2.58  | 1.72  | 1.78  | 2.14  | 2.35  | 1.79  | 1.67  | 1.98  |
| Br   | 0.187 | 0     | 0.25  | 0.19  | 0.01  | 0.0   | 0.24  | 0.22  | 0.17  |
| Sr   | 32.89 | 41.74 | 33.74 | 31.75 | 37.23 | 38.34 | 33.65 | 31.92 | 31.95 |
| Zr   | 2.45  | 3.88  | 2.65  | 2.27  | 3.24  | 3.56  | 2.6   | 2.4   | 2.4   |
| Nb   | 0.0   | 2.61  | 0.0   | 0.11  | 1.75  | 2.08  | 0.0   | 0.02  | 0.0   |
| Y    | 2.69  | 1.82  | 2.87  | 2.85  | 2.15  | 1.96  | 2.75  | 2.93  | 2.59  |
| Mo   | 0.016 | 0.38  | 0.18  | 0.15  | 0.28  | 0.35  | 0.17  | 0.17  | 0.15  |
| Cd   | 3.9   | 6.49  | 2.36  | 3.25  | 4.28  | 5.78  | 2.56  | 3.38  | 3.75  |
| Sb   | 0.33  | 0.0   | 0.22  | 0.37  | 0.12  | 0.0   | 0.25  | 0.39  | 0.31  |
| Ti   | 1.51  | 2.22  | 0.96  | 1.47  | 1.94  | 2.1   | 1.25  | 1.32  | 1.75  |
| MnO/Fe₂O₃ | 0   | -     | 0     | 0.08  | -     | -     | 0.28  | 0.12  | 0.69  |
| Cr/Zn | 0.85 | 0.23  | 0.77  | 0.85  | 0.21  | 0.21  | 1.12  | 0.77  | 0.88  |
| Ni/Zn | 0   | 0.03  | 0     | 0     | 0.02  | 0.02  | 0     | 0     | 0     |

RESULTS

Petrology and Mineralogy

The color of the chert ranges from in early light brown to black and dark gray is being most common. Bedded and concretions cherts are the main form occur as in an alternating manner with the limestone, while the brecciaed chert are less common forms, occurs in random distribution or parallel to the bedding planes. Nine representative samples were collected from the studied area. From the bottom to the top
of the sequence were investigated for major constituents of cherts are quartz with minor calcite and trace dolomite with apatite. The bedded chert forms show microscopically mosaic of microcrystalline, calcitic dolomitic calcite and phosphatic microcrystalline quartz where the brecciaed form is composed of angular and rounded heterolithic chert fragment in a silica cement, silica dissolution and replacement were observed in breccia and are mainly composed of calcitic, microcrystalline quartz. The concretion chert are composed of microcrystalline quartz and macrocrystalline quartz and minor chalcedony and a fewy calcitic. A small amount of replaced fossils were also found at concretion margins are growing at the expense of an adjacent carbonate. In general, the chert constituents are microcrystalline quartz. The dominant phase and minor calcite and variable occurrences of fossils fragment are throughout the microcrystalline, with a small amount of replaced fossil were also found, quartz groundmass. The calcitic microcrystalline quartz chert is extensively burrowed and contains a few fossils. Tests in groundmass show that the microcrystalline quartz. Ground mass contain spherical fossils compose of coarse grained quartz shrinkage structure, is characteristic feature of some studied thin section. The fossils microcrystalline quartz chert includes of fossils fragment scattering throughout microcrystalline quartz. These microfossils can be either filled with or replace by calcite or quartz in chert samples representing the different morphologies of silicification pattern where the silica replacement to original carbonates in early Diagenetic for concretion chert. The chert concretion and the surrounding carbonate were studied in order to interpret silica sources it could be produced by the secondary replacement of carbonates.

**Geochemistry**

The geochemical characterization of the chert formation occurs in Wadi Al-Wala have been analyzed for major and trace elements content Table (1). In spite of differences in appearance: color, luster and fracture; this chert have a quite similar composition with only significant differences in SiO$_2$ and CaO contents. The content of SiO$_2$ are usually larger than 90% or more the cherts are simple in petrochemical composition with a little amount, pure chert characterized high SiO$_2$ range from 61.18 – 97.30 wt %. The CaO of chert samples are distinguished by high of CaO contents particularly, in samples AsI 2 (22.67 wt %) and AsI 6 (17.95 wt %). In general, the CaO concentrations range between 0.65 and 22.67 wt % and show a negative correction with SiO$_2$ (Fig. 4). Fe$_2$O$_3$, MnO and P2O$_5$ show very slight variations. It is noticed that these oxides contents decreases as the SiO$_2$ concentration increase (Figs. 2, 3, 4, 5 and 6, respectively). The Ti contents are low and considered as a trace element. It
could be attributed due to the rejection from the parent rocks during the silicification processes of the cherts (Table 1).

![Fig. 2: Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} correlation diagram](image)

![Fig. 3: MnO-SiO\textsubscript{2} correlation diagram](image)

![Fig. 4: CaO-SiO\textsubscript{2} correlation diagram](image)
The total content of trace elements is considerably variable and low as compared with other worldwide occurrences (Knauth, 1994; Pen Jun et al., 2000; Al-Malabeh et al., 2004 and Brandle, 2016). In general, low contents of trace elements in chert samples may indicate its rejection during silicification. Pure cherts are characterized by high SiO2 and V contents (Fig. 7), and a small amount of other elements Cr (Fig. 8) is present in the studied chert samples which may indicate that the chert may be derived from seawater. High Zr and Sr (Figs. 9 and 10) content in pure chert and have a lower concentration in chert concretion, they show in general positive relationship between Zn and CaO. The trace elements such as Pb (Fig. 11), Bi, Ta, Se, Y, Ni (Fig. 12), Cd, Zr (Fig. 9) are variable in all chert samples. The concentration of these elements in chert
may lead to hydrothermal solution. This is further supported by the ratios of MnO/Fe₂O₃, Cr/Zn and Ni/Zn (Table 1). Moreover, the high by of most studied chert may support its genesis by silica replacement to carbonate original minerals. During the replacement processes most of the elements may be replaced by silica or mechanically rejected from the parent rock by silicification chert breccia's were formed by practically contemporaneous fracturing of lithified cherty layers followed by silicification and lithification of the matrix pairs of fragment and matrix were compared with respect to their chemical contents of CaO, K₂O, Sr, Mo, Cr, Zn K As, Zr and Cd may originate from hydrothermal solution.

![V-SiO₂ correlation diagram](image1)

**Fig. 7: V-SiO₂ correlation diagram**

![Cr-SiO₂ correlation diagram](image2)

**Fig. 8: Cr-SiO₂ correlation diagram**
Fig. 9: Zr-SiO$_2$ correlation diagram

\[ y = -0.0418x + 6.4606 \]
\[ R^2 = 0.9033 \]

Fig. 10: Sr-SiO$_2$ correlation diagram

\[ y = -0.2506x + 56.58 \]
\[ R^2 = 0.8917 \]

Fig. 11: Pb-SiO$_2$ correlation diagram

\[ y = 0.0298x - 0.1628 \]
\[ R^2 = 0.9723 \]
DISCUSSION AND CONCLUSION

The Upper Cretaceous chert in central Jordan occurs in the silicified limestone member of Amman Formation. It occurs as bedded, brecciaed and concretion forms alternated with or scattered throughout limestone and silicified limestone beds.

The chert are mainly consists of microcrystalline quartz, calcite microcrystalline quartz, fossils and phosphatic microcrystalline quartz. The bedded chert are composed almost entirely of microcrystalline quartz and secreting organism. These deposits are produced by compacting and recrystallizing of the organically produced siliceous ooze, deposits that accumulate on the present day abyssal ocean floor. The modern oozes gather in latitudes where high organic productivity of floating planktonic radiolarians and diatoms take place in the warm surface water some bedded chert might be of organic origin (Mohammad 1992; Knauth, 1994 and Mario, 1987).

Dissolved silica resulting from continental chemical weathering is the main contributing silica source initiating chert formation (Beauchamp and Baud, 2002; Manger, 2002; and Yuansheng et al., 2007). On the other hand, biogenic silica cannot be considered as the primary of silica source as chert formation can take place without the pressure of biogenic silica content. Groundwater also becomes enriched in dissolved silica. This lead to the secondary solidification process in permeable sediment of the coastal region and was on contact with marine phreatic waters. The explained of secondary chert formation in sedimentary rocks. Extensive mixing zones can arise by transgression-regression and tectonic uplift and-down faulting.
The Wadi Al-Wala chert locality has resulted in a major revision of the structure and stratigraphy of the area the main new structure elements recognized is a low angle extensional fault system which is perpendicular to Dead Sea fault system. The replacement origin of silica and the formation of chert were advocated by many authors for similar sequences (e.g., Blatt et al., 1979; Mario, 1987; Mohammad, 1992; Knauth, 1994; Owen et al., 1999; Peng Jun et al., 2000; Rice, 2004; Manger, 2002 and Yuansheng et al., 2007). It is proposed that many concretions chert in limestone have formed when mixing of marine and freshwater can produce water which was highly super saturated with respect to quartz and under saturated with respect to calcite (Murray, 1994 and Yongzhang et al., 2008). The origin of concretion chert are produced by the secondary replacement of the carbonate minerals and fossils with a shallow marine shelf deposits the main factors which control the solution and precipitation of silica phase are pH, temperature and CO$_2$ presence and the water turbulence the studied chert from Virginia suggested an additional source of silica is the volcanism associated with tectonic orogeny (Owen et al., 1999 and Kempe et al., 2006).

Also, volcanic silica sources as well as other subordinate silica sources cannot supply sufficient amounts of dissolved silica to explain extensive chert formation (Kolodny and Taraboulosi, 2006).

Field observations suggest that the breccia was formed by a process of syndetic limestone dissolutions another origin of concretion chert were produced by the secondary replacement of the carbonate mineral and fossil within shallow marine shelf deposits silica can be mobilized from elsewhere within a rock and transportation solution under proper condition of temperature and geochemistry (Al-Malabeh et al., 2002; Okurish and Matthes, 2005; Kolodny et al., 2005). The origin of silica through petrologic and geochemical evidence suggests a hydrothermal origin of the chert (Peng Jun et al., 2000; Yongzhang et al., 2008; Al-Malabeh and El-Hasan, 2009; Al-Fugha et al., 2012). In Wadi Al-Wala area, the trace elements indicate leaching of country rocks by hydrothermal solution and the evidence from hydrothermal origin include low MnO/Fe$_2$O$_3$, low content heavy metals low Cr/Zn and Ni/Zn ratios. For that, the petrologic and geochemical evidenced suggest a hydrothermal origin for Wadi Al-Wala chert.
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