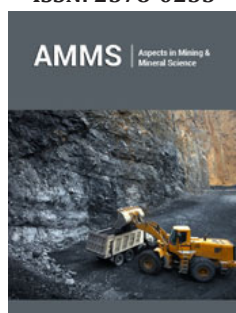


# Unique Minerals from the Varicolored Marble (Mottled Zone) of Central Jordan

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## Abstract

The recent work of the varicolored marble of central Jordan has indicated the presence of a diverse set of trace elements (Cd, Ce, Cu, Ni, Th, U, V, La, Nd, Ag, Zn, Zr, Sn, etc) in potential new accessory and minor minerals (oxides/sulfides/sulfates/silicates). The sulfides indicate its formation under reducing conditions. Sulfates, oxides, uranates, vanadates and silicates are indicative of combustion metamorphism under oxidizing conditions. The oxygen supply during combustion events has controlled the formation of the high temperature minerals. The circulating highly alkaline water has controlled alteration, leaching, mobility and formation of supergene secondary minerals along the weakness zones. The given mineralogical data have an important impact on natural analogues.

**Keywords:** Varicolored marble; New minerals; Mottled zone; Central Jordan; Tulul Al Hammam; Pyrometamorphism; Natural analogues; Natural cement

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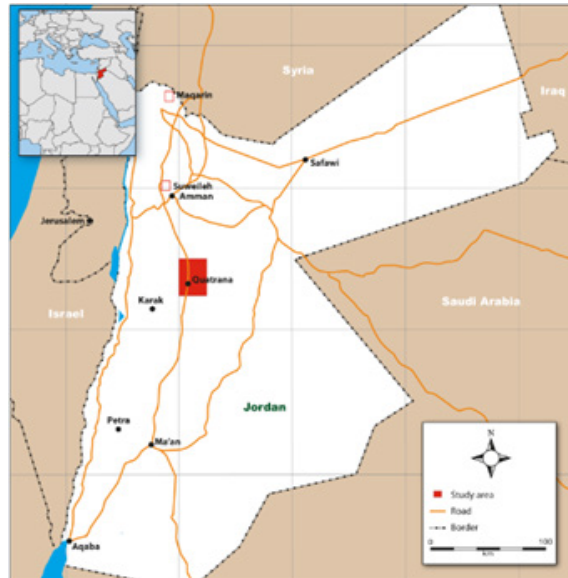
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## Introduction

The varicolored marbles (pyrometamorphic rocks) of central Jordan are widely distributed in Daba-Siwaqa area (Figure 1). The metamorphic rocks cover large areas of central Jordan and extend to more than 2000sq.km. The marbles are associated with kerogen-rich biomicritic bituminous marl/limestone, travertine and regolith. Organic matter (up to 30% in the biomicrite) has provided a significant potential for spontaneous combustion. Pyrometamorphism of the bituminous marl, the upper part of the Muwaqqar Chalk Marl Unit (MCM), has resulted in the formation of the varicolored marble that belongs to the sanidinite-pyroxenite-hornfels facies. High temperature minerals were formed as a result of spontaneous combustion metamorphism. Among these minerals are diopside, wollastonite, monticellite, gehlenite-åkermanite, spurrite and merwinite that confirm the event that is similar to that resulting from natural coal fires [1]. Similar events took place in the bituminous rocks of the mottled zone as indicated by the isochemical high temperature reactions and a mass loss of 30% [1-4]. Resulted varicolored marbles are highly heterogeneous in texture and color and are highly enriched in Redox Sensitive Elements (RSE) and Rare Earth Elements (REE) as Cd, Se, V, Cr, Ni, Cu, Ag, Zn, Th, U, La, Ce, etc [2]. These elements were inherited from the kerogen-rich biomicritic bituminous precursor. High temperature minerals were exposed to supergene alteration processes by the action of highly alkaline waters and have formed unusually low temperature minerals with unique chemistry and crystal structures. Wide range of new type locality minerals among others were discovered recently at Tulul Al Hammam site and other sites of central Jordan as indicated in Table 1. Orishchinite and Khurayyimite are among the most recently discovered new minerals. The varicolored marbles of central Jordan site were derived from the bituminous marl protolith as a result of pyrometamorphism. It is the lower part of the Muwaqqar Chalk Marl Formation that belongs to the upper part of the Belqa Group. The pyrometamorphic rocks crop out along the valleys and overlie the bituminous marl/limestone of the Muwaqqar Chalk Marl Unit (MCM) of Maastrichtian-Paleogene age. Pleistocene travertine, fluvial to lacustrine and Holocene to Present alluvium deposits overlie

unconformably the pyrometamorphic rocks [4]. Highly alkaline water was responsible for leaching and liberation of the Reduced Sensitive Elements (RSE) and the subsequent precipitation and incorporation of these elements in the supergene low temperature

minerals along the weakness zones in travertine. The interaction of such leachate with surrounding rocks and the mobility of radionuclides in this complex system must be considered in repository safety assessment [5].



**Figure 1:** Location map of the varicolored marble, Central Jordan.

**Table 1:** Type locality and valid high and low temperature minerals from the pyrometamorphic zones (natural analogues/ cement zones) of central Jordan+, Maqarin\* and Suweileh areas# [1-4]. **Bold Italic:** New type locality valid minerals identified by foreign researchers not related or connected to the active national University of Jordan research team (The University of Jordan team is currently working on the same location since 1982). **Bold:** Preliminary SEM/EDS results of potential new minerals [1].

Minerals	General Formulae
<i>Orishchinite</i> +	<b><i>(Ni<sub>1.04</sub>Fe<sub>0.64</sub>Mo<sub>0.31</sub>Co<sub>0.01</sub>)Σ2.00P</i></b>
<i>Nickolayite</i> +	<b><i>FeMoP</i></b>
<i>Transjordanite</i> +	<b><i>Ni<sub>2</sub>P</i></b>
Cd-rich sphalerite+	(Zn,Cd)S
Cu-richdjerfisherite +	K <sub>6</sub> Na(Cu,Fe,Ni) <sub>25</sub> S <sub>26</sub> Cl
Sphalerite+	(Zn,Cd,Fe)(S,O,Se)cub
Sphalerite+ with thiozincate phase	ZnS (Cd-rich) or bearing (Na,K,Ba) or with Na <sub>2</sub> Zn <sub>4</sub> S <sub>5</sub>
Cu-K-Na-Selenide*	Cu <sub>10.2</sub> K <sub>3</sub> Na <sub>0.2</sub> Se <sub>7.7</sub> S <sub>2.3</sub> (approx.)
Unidentified phase +	Fe-Ni-Cu -Cr-Zn-Mo-Ba-S-Se
Ba-Sr phase+	(Ca, Ba, Sr)10- <sub>x</sub> [(SO <sub>4</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> ](F-, O <sub>2</sub> -, Cl-) <sub>2</sub> (1<X<2)
Unidentified Na-sulfate-phosphates+	Na-(SO <sub>4</sub> )-(PO <sub>4</sub> )
Unidentified phase +	Ca-aluminate
Ag-Cerianite+	(Ce,Ag)O <sub>2</sub>
Lime-monteponite solid solutions+	(Ca,Cd)O
Tululite+	(Ca,Cd) <sub>4</sub> (Fe <sub>3</sub> +Al)(Al,Zn,Fe <sub>3</sub> +Si,P,Mn,Mg) <sub>15</sub> O <sub>36</sub>
Undefined multiple element ferrites*	(Ca,Ba,Ti,Mg,Zn,Mn)(Fe,Al,Cr) <sub>2</sub> O <sub>4</sub>
<i>Priscillagrewite-(Y)</i> +	<b><i>YCa<sub>2</sub>Zr<sub>12</sub>Al<sub>3</sub>O<sub>12</sub></i></b>
<i>Mconnellite</i> +	<b><i>CuCrO<sub>2</sub></i></b>
<i>Ellinaite</i> +	<b><i>CaCr<sub>2</sub>O<sub>4</sub></i></b>
Vapnikite+#	β-Ca <sub>3</sub> UO <sub>6</sub>
Vorlanite + #	(CaU <sub>6</sub> +) <sub>4</sub>

"Protovorlanite" + #	CaUO <sub>4</sub> rhombohedral (R3m)
Unidentified phase+ #	α-Ca <sub>3</sub> UO <sub>6</sub> rhombohedral(R3 )
Unidentified phase+ #	Ca <sub>2</sub> UO <sub>5</sub>
Unidentified phase+ #	Ca <sub>4</sub> UO <sub>7</sub>
Unidentified phase+ #	Ca <sub>5</sub> UO <sub>8</sub>
Unidentified phase+ #	Ca <sub>6</sub> UO <sub>9</sub>
Unidentified phase+ #	Ca <sub>3</sub> U <sub>2</sub> O <sub>9</sub>
Unidentified phase*	Ba-Ca-sulphate-silicate
Unidentified phase*	Ba-Ca-Zr-Mo-silicate
Unidentified phase+	Ca-U silicate
<b>Khurayyimite+</b>	<b>Ca<sub>7</sub>Zn<sub>4</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(OH)<sub>10-4</sub>H<sub>2</sub>O</b>
<b>Qatranaite+</b>	<b>CaZn<sub>2</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub></b>
Ca[OH]2 - Cd[OH]2 solid solutions+	(Ca <sub>0.67</sub> Cd <sub>0.33</sub> )[OH] <sub>2</sub> - (Ca <sub>0.45</sub> Cd <sub>0.55</sub> )[OH] <sub>2</sub>
Cd-basic chloride+	Cd(OH) <sub>2</sub> -XCIX
Unidentified phase*	Fe oxyhydroxides
Hashemite+	Ba(CrO <sub>4</sub> )
Unidentified phase*	Cd-sulfate
Unidentified phase*	Cu,Zn-sulfate
Unidentified phase*	Pb-sulfate
<b>Siwaqaite+</b>	<b>Ca<sub>6</sub>Al<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O</b>
Unknown CSH-U+6 phase+	(CaO) <sub>3</sub> (UO <sub>3</sub> ) <sub>2</sub> (SiO <sub>2</sub> ) <sub>2.5</sub> ·6H <sub>2</sub> O
Volkonskoite+ # (SS)	Ca <sub>0.3</sub> (Cr,Mg) <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O
Tyuyamunite -Strelkinite SS+	Ca(UO <sub>2</sub> ) <sub>2</sub> (VO <sub>4</sub> ) <sub>2</sub> ·5-8H <sub>2</sub> O - Na <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (VO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)
X-Phase+	Ca <sub>2</sub> UO <sub>5</sub> ·2-3H <sub>2</sub> O
<b>Potential new phase+</b>	<b>(FeCa) alloy</b>
<b>Potential new phase+</b>	<b>(CaSi) alloy</b>
<b>Potential new phase+</b>	<b>KZn(Cu,Fe)-sulfide</b>
<b>Potential new phase+</b>	<b>KCuCa-sulfate</b>
<b>Potential new phase+</b>	<b>FeCa(CrNi)-oxide</b>
<b>Potential new phase+</b>	<b>CaFeAl(TiZn)-oxide</b>
<b>Potential new phase+</b>	<b>CrMg(ZnAlFe)-oxide</b>
<b>Potential new phase+</b>	<b>Ca(LaCeNd)Th-oxide</b>
<b>Potential new phase+</b>	<b>F--rich Ca-uranate</b>
<b>Potential new phase+</b>	<b>Ce(U)Ca-vanadate</b>
<b>Potential new phase+</b>	<b>MgAl(CaFe)-silicate</b>
<b>Potential new phase+</b>	<b>CaCd-silicate</b>

The combustion model is supported by the depletion of the heavy stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) from the carbonates of the varicolored marble (strongly enriched in light isotopes of oxygen and carbon [6,7]. A mud-volcanic hypothesis was suggested to replace the spontaneous combustion model but is still under debate. Meteoritic impact model is recently proposed as a triggering event of combustion, in addition to the previously known spontaneous combustion and tectonism along the Jordan Rift Valley models [1]. A recent work on the varicolored marble [5] has revealed a continuous discovery of unusual and unknown minerals with unique crystal chemistry. Preliminary SEM/EDS results of the varicolored marbles of Tulul Al Hammam site in central Jordan have indicated potential new phases as (Fe,Ca), (CaSi) metallic alloys, KZn(Cu,Fe,Ca)-

sulfide. The FeCaCr(Ni)-oxide phase is a mixture between Fe and Cr minerals (15% Cr+Ni) and Cd(Ca)-silicate phase is altered to CaAlCd-silicate. A KCuCa-sulfate phase altered to NaK(Na)Cu(Ca)-sulfate, ThCa-sulfate, CaFeAl(TiZn)-oxide, Cr(Al)Mg(Zn)(Fe)-oxide, Ca(LaCeNd)Th-oxide and Ce(U)Ca-vanadate phases are among the potential new phases [1]. A Ca-uranate phase with high fluorine content (18.5%) is a new variety to be added to the 1- 6 Ca:U molar ratios phases [8,9].

Disseminated oxides and sulfides of the trace elements in the varicolored marble indicate reducing/oxidizing conditions. The oxygen supply during combustion has controlled the radicals. Sulfates for example are indicative of combustion metamorphism

under oxidizing conditions, when sulfur ( $S^{2-}$ ) in primary disseminated sulfide minerals and organic matter was oxidized up to the highest valence ( $S^{6+}$ ). The formation of oxides, sulfides and/or sulfates of Cr, Zn, Cd, Ni, Cu, etc during the combustion events was mainly governed by local redox conditions. Conversion of sulfide sulfur to sulfate occurred by oxidative combustion of dispersed S-rich protolith and the liberation of metals bound to the original sulfides and organic matter. All these phases are indicative of formation under reducing/oxidizing conditions as a result of combustion metamorphism [4]. The oxygen supply during combustion was the controlling factor for the formation of the oxides, sulfides and/or sulfates of the RSE and REE. During the combustion events high temperature sulfides were mainly governed by local redox conditions. Conversion of sulfide sulfur to sulfate occurred by oxidative combustion of dispersed sulfur ( $S^{2-}$ )-rich protolith to ( $S^{6+}$ ), followed by the liberation of metals bound to the original sulfides and organic matter. The following abstracted review on central Jordan pyrometamorphic sites give real-world insights into the outcome of natural analogues modeling results to verify its accuracy [10-14].

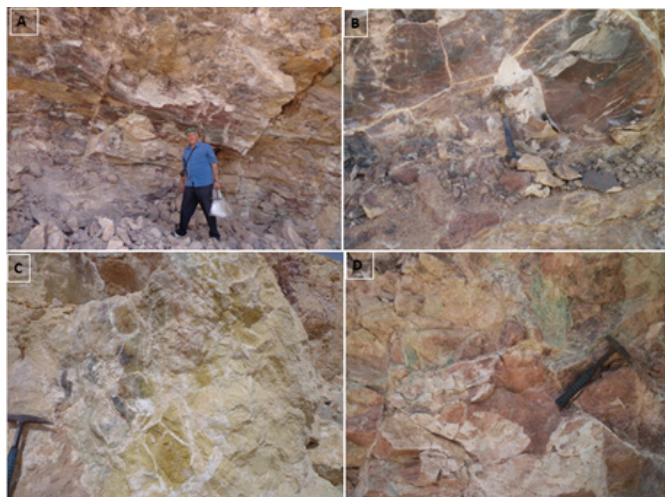
### Geology and Chemistry of the Varicolored Marbles in Central Jordan

The geology, stratigraphy and sedimentology of central Jordan are described in detail by the Natural Resources Authority (NRA) reports [7,15]. The main geological feature in the area is represented by the Muwaqqar Chalk Marl Unit (MCM) that consists of bituminous marl (known as oil shale), chalk and marly limestone with some concretions. The northeastern part of Daba-Siwaqa area forms cliffs and hills known as Tulul Al Hammam and is related to the tectonism of the Jordan Rift Valley, located ~60km to the west of the area. The exposed sedimentary rocks in central Jordan range in age from Upper Cretaceous (Turonian) to Tertiary (Eocene). The Bituminous Marl Formation overlies El-Hasa Phosphorite Formation (Campanian-Maestrichtian age) and underlies Umm Rijam Chert Limestone Formation (Eocene age). The El-Hasa Phosphorite Formation is composed of phosphates, phosphatic chert and limestone, chert, coquina and marl. Gentle folding and faulting are mostly related to the continuous tectonic activities that are still active along the Jordan Rift Valley. Folding is related to the regional compression, occurring adjacent to faults directly associated with drag during faulting, and is the result of interference structures caused by the interaction of dominating E-W and NW-SE fault influences. The main faults in the area are the Zerqa Main, Daba and Siwaqa fault systems. Another fault set is an E-W group of faults and linear features. The metamorphic rocks in central Jordan are highly fractured and brecciated and are characterized by the presence of molten rocks and polygonal structures. Central Jordan is stratigraphically and lithologically similar to the mottled zone of Israel and the west bank of Jordan. The kerogen-rich biomicritic bituminous beds of the Muwaqqar Chalk Marl/Limestone Formation (MCM) are characterized by unusual high enrichment of Redox Sensitive Elements (RSE) and Rare Earth Elements (REE). During the late Cretaceous to early Eocene (~90 -

~50Ma ago), Jordan was situated in a shallow marine, stable shelf environment of the Tethys Sea. The sea water was enriched with an exogenic metal flux leached from the Troodos and Baer Bassit ophiolite [16]. Trace elements are especially abundant and diverse in immature organic-rich siliceous marl. The abnormal and extreme polymetallic enrichment of RSE and REE of the bituminous marl is related to extremely high bioproductivity (planktons were the key agent in selective re-distribution of P, Si and RSE) of the upwelling zone in the southern Neo-Tethys margin coupled with euxinic depositional environments. The biomicritic bituminous marl is rich in bioclasts and planktonic foraminifera. Calcite is the major component while carbonate-rich fluorapatite (francolite), quartz, goethite and dolomite are essential constituents and framboidal pyrite fills foram cavities [2]. The average sulfur content is 1.15% and the RSE are present in the bituminous marl as sulfides, sulfosalts and selenides. Native selenium, calcium-strontium sulfates and selenates are also present. In addition to pyrite, traces of Zn-Cu-Ni-Fe sulfides, sulfosalts and selenides, Ca-Sr sulfates and selenates, framboidal sphalerite, galena, Ni-selenide, Ag-selenide, Ag-Cu-Ni-Fe-Zn-Cd sulfides and selenides, REE and oxides are also present. The major chemical components include among others CaO, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>. The average concentrations (ppm) of some RSE and REE as Cu (115.0), Ni (139.0), Mo (94.0), Th (10.0), U(25.0), Y(27), Zr (46.0), Cr (267.0), V (268.0), La (28.0), Zn (451.0) are relatively high. The bituminous marl from Siwaqa area, however, has the highest mean ppm values of Zn (4695), U (2176), V (727), Mo (496), Ni (448), Cr (418), and Cd (197) [16,17]. The varicolored marbles range in color from black and brown to red, pink, and green, depending on their mineralogical composition and the degree of supergene alteration. Pyrometamorphism of the bituminous marl has led to enrichment of the RSE of the varicolored marble. The gray, green apatite rich and brown marbles were derived from the bituminous calcareous, phosphatic and argillaceous precursors. The CaO, P<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub> contents of the three varieties are 47.75%, 22.34% and 5.03% respectively. The high SO<sub>3</sub> content (10.14%) in some of the brown marble samples is attributed to the presence of secondary supergene minerals such as ettringite. The gray marble has the highest Sr (7262ppm substituting for Ca) and Zr (159ppm) content. The brown marble has the highest Zn (1763ppm), V (346ppm) and Cr (4319ppm) values. The green apatite marble has the highest Ba (467ppm) and Cu (261ppm) values [4]. The fresh varicolored marbles, however, are the richest in REE (ΣREE mean value=69ppm, ΣREE maximum value=218ppm). The ΣLREE form 90% of the ΣREE with the predominance of La and Ce (70%) [3].

The unmetamorphosed rocks have an isotopic composition in the range of normal marine carbonates and are strongly enriched in light isotopes of oxygen and carbon. The green phosphate-rich samples average  $\delta^{18}OPDB=6.8\%$ ; dark gray apatite-rich samples average  $\delta^{18}O=-10\%$ ; violet apatite-rich samples average  $\delta^{18}OPDB=-12.4\%$ . The travertine in central Jordan and Maqarin is highly depleted in  $\delta^{13}C$  values as low as -25.45%. The stable isotopes ( $\delta^{18}O$  and  $\delta^{13}C$ ) were depleted from the carbonates (recrystalline calcite, spurrite and larnite). The isotopic depletion in  $\delta^{18}O$  and  $\delta^{13}C$  from equilibrium values and the active metamorphism in analogous

area at Maqarin, north Jordan supports the thermal event. The enrichment in light isotopes is related to the rapid uptake of light oxygen and carbon isotopes from the atmosphere and from the oxidized organic matter during the combustion and recarbonation processes [7,9].



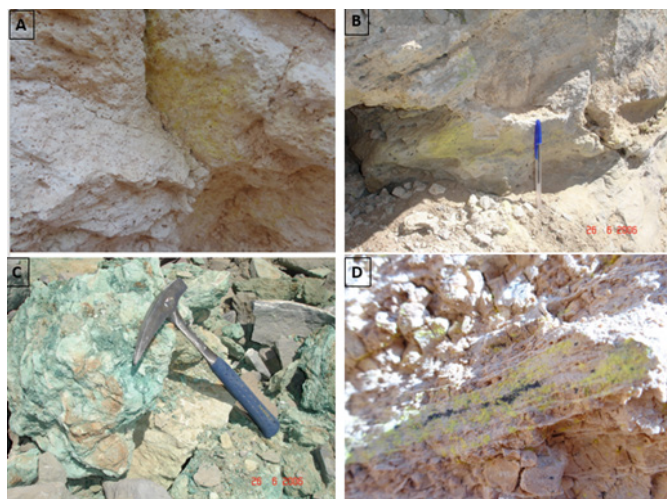
**Figure 2:** Field photographs of the varicolored marble (pyrometamorphic rocks) (A) highly fractured and brecciated (B) The fresh black variety at the center grades into brown marble (C) yellow highly brecciated, altered and fractured, filled with secondary minerals (D) fractured and partially altered, with secondary mineralization. The green and white encrustations are volkonskoite and calcite.

### Mineralogy and Chemistry of Central Jordan

The recently exposed walls of the quarries at central Jordan have fresh massive outcrops, indicating the original textures and structures of the sedimentary precursor beds. Fresh samples are homogeneous, massive, and crypto- to micro- crystalline (up to 50 $\mu$ m) and often show thin bands up to 3cm of alternative colors that reflect uneven distribution of sulfides and phosphate minerals in the parent rocks. The fresh black marble alters to brown variety and the more altered varieties alter to pale red or pink and are rich in disseminated sulfides. The green varieties are rich in fluorapatite and ellestadite, and the brown varieties are rich in fresh Ca-ferrites. In fractured and brecciated zones, the varicolored marbles are strongly hydrated, and high-temperature minerals are partially or totally altered to secondary Ca-carbonate, CSHs, CASH and sulfate minerals. Figure 2 shows field photographs of highly fractured and brecciated varicolored marbles (pyrometamorphic rocks). The intensively fractured altered samples show different degrees of hydration as a result of interaction of the circulating highly alkaline water with the fractured pyrometamorphic rock. In these zones, trace elements, namely U and Cr, are redistributed and segregated into rich independent areas of mineralization. Volkonskoite, "Uranmicas" and ettringite among others occur either as encrustations, impregnations, or filling materials in joints, cavities, and other permeable zones [7,9].

The high temperature minerals of the varicolored marble are the result of recrystallization-decarbonation-dehydration processes. Pyrometamorphism of cherty bituminous marl/limestone has produced larnite, spurrite, wollastonite, bituminous phosphate-rich marl has produced carbonate-rich fluorapatite (with S, Si) and ellestadite, and bituminous marl has produced silicates and oxides as fluormayenite, dorrite, tilleyite, brownmillerite, K-rich ternesite, calcsilicates, ye'elimite, calc-aluminates, garnet, chrome-ferrite phases, lime, Ca-U+6 oxide minerals [3,4]. The low temperature minerals are the result hydration-carbonation-sulfurization-replacement reactions and alteration. Secondary minerals are found filling voids, cavities and fractures that indicate later multi-stage reactions with the highly alkaline circulating water (pH~12.7). Among the low temperature minerals are calcite, K-rich member of the apophyllite group  $KCa_4Si_8O_{20}(F,OH).8H_2O$ , gypsum, afwillite, Cr-Sr rich ettringite and gypsum (violet and green), thaumasite, portlandite (Cr-rich), vaterite, birunite, Al-tobermorites, barite-hashemite-celestite, zeolites, Zn-Cd sulfide/selenide, fluorite, X-phase  $Ca_2UO_5 \cdot 2-3H_2O$ , hematite, hillebrandite, foshagite, katoite, hydrocalumite, brucite, siwaqaite, qatranaite [7,9]. Pleistocene travertine is widely distributed to the south of Siwaqa fault and overlies the varicolored marble at central Jordan. It is yellow brown-wavy vesicular and banded, mainly composed of micro- to cryptocrystalline calcite with lot of opaline phases (opal-CT), sulfates-chromates (gypsum, hashemite and ettringite), and mineralized plant remains (Figure 3). Some of the travertine is colored (green and yellow) as a result of secondary precipitation of Cr-rich smectite (volkonskoite) and "uranmica" (tyuyamunitestrelkinite). Highly alkaline circulating waters have precipitated soft travertine and secondary low temperature minerals along the weakness zones of the varicolored marbles and the rocks below as a result of kinetic reaction of the hydroxide waters with atmospheric CO<sub>2</sub>. The rapid uptake of atmospheric CO<sub>2</sub> has resulted also in the high enrichment of light isotopes of oxygen and carbon [7]. Recent regolith layers cover the varicolored marble and/or travertine and in many cases are associated with yellow, white and green encrustations that correspond to "uranmicas", calcite and green Cr-rich smectite-volkonskoite. Spary cactite filling fractures, vugs and cavities are widely distributed along the weakness zones [7,18,19]. The mineralogy and chemistry of central Jordan sites are similar to other localities in central Jordan. Anhydral calcite crystals appear relatively large (up to 200 $\mu$ m). The metallic minerals vary from single crystals  $\leq 2-20\mu$ m up to clusters of numerous crystals reaching  $>200\mu$ m. Most of the studied marbles consist up to 90% calcite, 15% carbonate- fluorapatite, 5% spurrite, and 3% brownmillerite, as well as sporadic crystals of Ca-ferrites, mayenite supergroup minerals, and accessory and minor phases of Zn, Cd, Ni, Cu, Ag, and U as Zn-rich periclase, tululite, lakargiite, srebrodolskite, periclase (Zn-, Ni-, Co-, and Cu-rich), lime-monteponite  $[(Ca,Cd)O_{ss}]_2, Ca_{1-x}Cd_x(OH)_2$ , Ca-uranates with Ca:U molar ratios from 1 to 6, spinel (Fe-Zn bearing), cassiterite SnO<sub>2</sub>, cerianite (Ce,Th,Ag)O<sub>2</sub>, oldhamite, (Mg,Ni,Ca,Zn,Cd) oxides, multiple element ferrites (Fe, Cr, Ti, Al oxides), zincite ZnO (Cd-bearing), greenockite, acanthite

, pyrrhotite, sphalerite (Fe- and Cd-bearing) associated with thiozincate phase, samaniite, and Cu-rich djferfisherite, galena, chalcocopyrite, barite, hashemite, ettringite, bentorite, thaumasite, volkonskoite, tyuyamunite and strelkinite, etc [4]. The varicolored marbles are rich in RSE and REE concentrations [2,17,18]. Oxides/sulfides/silicates of a wide diversity of trace elements composition as redox sensitive elements RSE (Cu, Ti, V, Cr, Fe, Mn, Zn, Pb, Ni, Co, etc) and REE are among the identified minerals in central Jordan.



**Figure 3:** Field photographs of porous travertine with secondary mineralization of: (A, B) yellow uranmica minerals along the weakness zones (C) green volkonskoite (D) yellow uranmica minerals and dark green Cr-rich phases filling the pores and cavities.

Central Jordan varicolored marbles are inherited from Muwaqqar bituminous marl (oil-shales) precursor and are converted to high temperature minerals. Supergene alteration processes by the action of highly alkaline circulating water was responsible for the formation of the low temperature minerals. The major- and trace-elements of the bituminous marl (the protolith) and the varicolored marbles (formed by spontaneous combustion) are similar. The distribution of Redox Sensitive Elements (RSE) and Rare Earth Elements (REE) in both bituminous marl and the varicolored marbles show high to moderate concentrations in the form of sulfides and selenides [7,9]. The pyrometamorphism induced by the combustion (the burning of the initial organic matter) of the bituminous marl and the volume loss as a result of decarbonation allowed the mobilization and enrichment of RSE and REE in the varicolored marbles. The combustion of the organic-rich source rocks has formed high temperature minerals with unusual chemistry. The identified minerals in central Jordan indicate the presence of oxygenated and reduced compounds because pyrometamorphism needs air oxygen as an oxidant to keep the combustion and the liberation of trace elements [19,4]. The circulating highly alkaline water has accelerated the leaching processes of the RSE and the fractionation of LREE mainly La and Ce [2]. The mobilization of leached elements from their host was followed by its incorporation in the structure of low temperature minerals. The oxidizing conditions are indicated by the presence

of abundant oxidized elements such as  $\text{Cr}^{6+}$  in ettringite, bentorite, hashemite, etc,  $\text{V}^{5+}$  and  $\text{U}^{6+}$  in vanadates (tyuyamunite and strelkinite) and other metal oxides.

## Conclusion

The high concentration of the RSE and REE is reflected by the chemistry of the high temperature minerals of the fresh varicolored marbles and the supergene low temperature minerals hosted by the altered varicolored marbles, travertine and regolith. The pyrometamorphic varicolored marbles of central Jordan offer the best natural sites that mimic the environmental conditions where cement is used. The unusual chemistry of the potential new minerals indicates that they act as a sink for hazardous elements in natural analogues.

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## Author Contribution

The manuscript text, photos, figures and analytical data were accomplished by the author. All the original data files are available at request from the author.

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