Determination of the Trace Elements Effecting The Color of the Gypsum Mineral

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Abstract— **Gypsum is the chemical sedimentary rock and wide spread in Turkey and the World. Gypsum may have different colors like white, gray, pink and orange.**
In this study, trace elements in white gypsum collected from Ulukışla Evaporites (Central Turkey) and trace elements in orange gypsum collected from Ostradnaya (Russia) were investigated. As a result of the evaluation of the obtained data, it is found that, the elements that give the orange color to the gypsum are Fe, Cr and Ni.

Index Terms— **Gypsum, Geochemistry, trace elements, color**

I. INTRODUCTION

Gypsum (calcium sulfate) is commonest of the natural sulfate minerals. Gypsum, $CaSO_4$-$2H_2O$, contains 27% water; anhydrite, $CaSO_4$, is the anhydrous form. In between is metastable mineral bassanite, $CaSO_4$-½ H_2O, or natural stucco (1). Gypsum is found in nature most commonly as the sparingly soluble salt $CaSO_4.2H_2O$, and often coexists with calcite (2, 3). The concentration of a saturated solution of gypsum is about 15 mM, and so is more soluble than calcite which typically gives in soil solution a concentration of between 1 and 10 mM Ca^{2+} depending on pH and partial pressure of CO_2 (4). Gypsum forms as a low-temperature hydrothermal mineral, crystallizing from meteoric water circulating in sandstone and clays, but major occurrence of the mineral is in evaporite deposits. As a solution becomes supersaturated, gypsum, anhydrite, and halite precipitate out consecutively and from alternating layers of these minerals. Gypsum also grows on the surface of clay or sand grains, and exhibit a flower-like morphology (desert roses) (5). Both gypsum an anhydrite occur in granular, compact or fibrus crystalline masses in sedimentary beds; common associates are dolomite and shale. Elementary distribution of the pure gypsum (weight %) is Ca: 23.28, H: 2.34, S: 18.62 and O: 55.76 (Table 1). But it is not possible to find a pure gypsum mineral in nature. Some contaminant elements enter the structure of gypsum while it was occuring and cause physical and chemical changes. This impurities constitute the centers of crystallization and recrystallization of gypsum, which thus develops granoblastic, occasionally porphyroblastic texture. Coarse-grained gypsum contains more impurities than the fine-grained variety. Less common forms of gypsum include selenite, which as large, clear monoclinic crystals in fluid-filled spaces or in an easily deformable host material; satin spar, a fibrous secondary stress mineral that develops during deformation as fracture filling with needles perpendicular to the fracture walls; and alabaster, fine-grained and compact, wich has long been used for carving into various art objects (6). Four distinct physical theories (formalisms) are required for complete coverage in the processes by which intrinsic constituents, impurities, defects, and specific structures produce the visual effects we designate as color (5).

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Table 1

1.1. Trace elements in Ca sulfates

Minor and trace elements can be incorporated into gypsum or anhydrite by the following processes (7):
substitution for Ca^{2+} in the $CaSO_4$ lattice;
adsorption due to electrostatic attraction.
Adsorption and inclusion mechanism cannot easily be predicted. However, substitution of a trace element for Ca^{2+} in the $CaSO_4$ lattice is controlled by distribution coefficients and the element/Ca ratio of brine, which precipitated the gypsum, as expressed by the following equation;
$(Tr/Ca)_G = K_d\ (Tr/Ca)_B$ (*1*)
Tr represents trace element. $(Tr/Ca)_G$ is the molar ratio of trace element to Ca in Gypsum. $(Tr/Ca)_B$ is molar ratio of trace element to Ca in brine, which precipitated the gypsum. K_d is the distribution coefficient for the trace element between gypsum and brine. Assuming substitution for Ca dominates trace elemnt incorporations in gypsum, element/Ca ratios of ancient brines can thus be estimated based on analyzed lattice-bound element concentrations from gypsum and distribution coefficients from Eq (*1*).
Adsorption and inclusion are randomly distributed in gypsum cyristals and hence are out of our control. For a process of substitution of trace elements for Ca^{2+}, the incorporated concentrations of trace elements into the gypsum lattice are controlled by distribution coefficients and the elements/Ca ratios of brine which precipitated the gypsum. Therefore, elements/Ca ratios of ancient brines can be estimated based on lattice-bound element concentrations from gypsum and distribution coefficients.
In this study, geochemical data obtained from analysis made on the white colored gypsum samples of Ulukışla Evaporites and orange colored gypsum samples collected from Ostradnaya (Russia) region and trace elements that give orange color to gypsum were evaluated. As a result of this evaluation, which trace elements made the gypsum colored were determined.

II. Material – Method

Gypsum samples that is subjected to this study were collected from Ulukışla (Nigde-Central Turkey) Evaporites and Ostradnaya (Russia) region. Ulukışla Evaporites are located at the south of Central Anatolia, east of Nigde City. South of the Maastrichtien - Upper Eocene aged Ulukışla Basin (8) is bounded by Bolkar Carbonate Platform, at the northeast by Nigde Massive, at the east by Aladağlar and Ecemiş Fault.
To avoid the possible pollution that can be occured in surface conditions, studies were carried out on the preserved parts of the samples that don't have any cracks or fractures. 3 of the samples are white colored (Samples; 1, 2 and 3) (Figure 1), the sample collected from Ostradnaya (Russia) is orange colored (Sample no 4) (Figure 1). Trace element analysis of the samples were determined by ICP method in Canada ACME Laboratories. In addition, to determine the mineral paragenesis of the sample 1 (white gypsum) and sample 4 (orange gypsum), XRD analysis were carried out in TUBITAK-MAM laboratories. To determine the crystal structure and shapes of these 2 samples, microphotographs were taken in Hacettepe University Geological Engineering Department with ZEISS evo 50 model SEM machine (20-30 kv voltage, 2,8 A current, x300 magnification).

Figure 1.

III. Results and Discussion

In this study XRD analysis were carried out on each white and orange colored gypsum samples. (Figure 2 and 3). According to the results, d (Å) values are as follows: sample 1; 7,60856 A°, 4.28722 A°, 3.80213 A°, 3.06682 A°, 2.87397 A°, 2.68468 A°, 2.21891 A°, 2.08423 A° and 1,89975, sample 4; 7.57970 A°, 4.27686 A°, 3.79531 A° and 3.06182 A° (Table 2 and 3). According to d (Å) values, both samples (white and orange) are gypsum minerals.

Figure 2.
Figure 3.
Table 2.
Table 3.

Gypsum minerals show generally massive view in SEM photographs (Figure 4 and 5). Although there are disintegrations and fine sticky particles in breaking surfaces, they have conchoidal breaking surfaces in general. The reasons of these properties are related both with the chemistry and physical structure of the gypsum samples. As seen in SEM photographs, the sample consists of one mineral and some tabular pieces in geometric structure were observed by the effect of fractures at the surfaces. Both the orange colored gypsum sample and the white colored gypsum sample represents structurally the same properties.
As a result of the SEM studies of the samples (Sample no 1 and 4) it is observed that crystals are wholly locked together and have compact structure. The sides that form the crystal dimensions have smooth planes and they have a dimensions of approximately 50x200 µm for both samples (Figure 4 and 5).
Trace element analysis results (ppm) for 3 white gypsum samples (Sample no 1, 2 and 3) and 1 colored gypsum sample (Sample no 4) are as follows; for sample no 1; Si: 650, Sr:772, Mg: 20, for sample no 2; Si:930, Sr: 907, Mg: 60, for sample no 3; Si: 690, Sr:696 and for sample no 4; Si:740, Sr:1145, Fe: 455, Mg: 180, Cr:12 and Ni: 30 (Table 2). Si and Sr elements are common in all of the samples, Mg element was determined in white gypsum samples no 1, 2 and colored gypsum sample no:4. Unlike white colored gypsum samples, Fe, Cr and Ni elements were determined in colored gypsum sample (Table 2).

Figure 4.

Figure 5.

Table 4.
According to the geochemical analysis results, while there are no Fe, Mg, Cr, Ni in white colored gypsum, there are Fe (455 ppm), Mg (180 ppm), Cr (13 ppm) and Ni (30 ppm) in colored gypsum. Si and Sr are the common elements in both white and orange colored gypsum samples. The ratios of these common elements are approximately equal.
As a result of the evaluation of the obtained data; it is thought that the elements that give the orange color to gypsum are Fe, Mg, Cr and Ni. Further detailed investigations can be on the subject about how effective these elements that give color to gypsum are.

References

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Table 1. Elementary distribution of the pure gypsum (weight %).

Element	Weight %
Calcium (Ca)	23.28
Hydrogen (H)	2.34
Sulfur (S)	18.62
Oxygen (O)	55.76
Total	100.00

Table 2. 2θ and d(Å) values for sample 1 (white gypsum).

2 θ (deg)	**d (Å)**	**Intensity**	**Mineral**
11.6213	7.60856	100	Gypsum
20.7015	4.28722	73	Gypsum
23.3777	3.80213	21	Gypsum
29.0938	3.06682	62	Gypsum
31.0937	2.87397	33	Gypsum
33.3478	2.68468	23	Gypsum
40.6265	2.21891	11	Gypsum
43.3800	2.08423	11	Gypsum
478418	1.89975	10	Gypsum

Table 3. 2θ and d(Å) values for sample 4 (orange gypsum).

2 θ (deg)	**d (Å)**	**Intensity**	**Mineral**
11.6657	7.57970	100	Gypsum
20.7522	4.27686	29	Gypsum
23.4203	3.79531	19	Gypsum
29.1423	3.06182	32	Gypsum

Table 4. Trace elements analysis results of the samples (ppm)

	ppm			
Sample No /Element	**1**	**2**	**3**	**4**
Si	650	930	690	740
Sr	772	907	696	1145
Fe	-	-	-	455
Mg	20	60	-	180
Cr	-	-	-	13
Ni	-	-	-	30

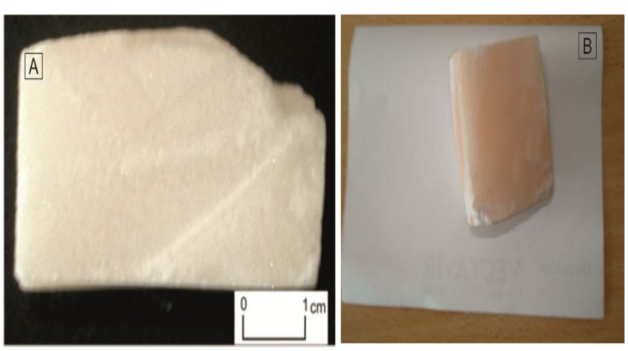

Figure 1. Gypsum samples (A: White colored gypsum with XRD and geochemical analysis; B: Orange colored gypsum with XRD and geochemical analysis).

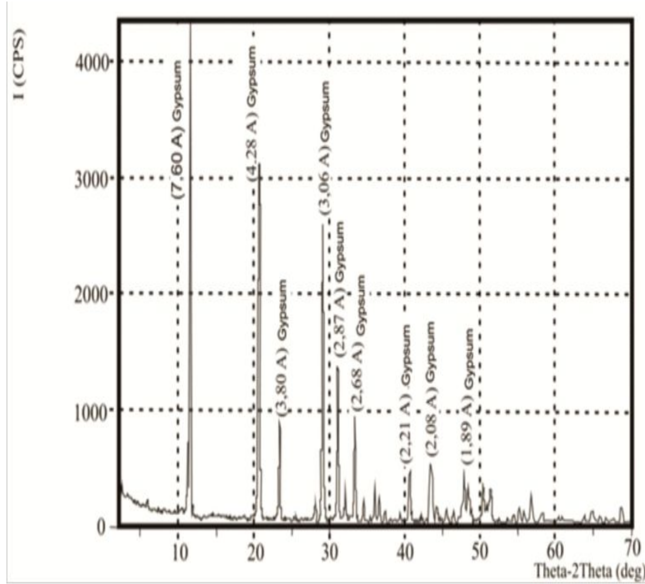

Figure 2. XRD diffractogram for the sample 1 (white gypsum).

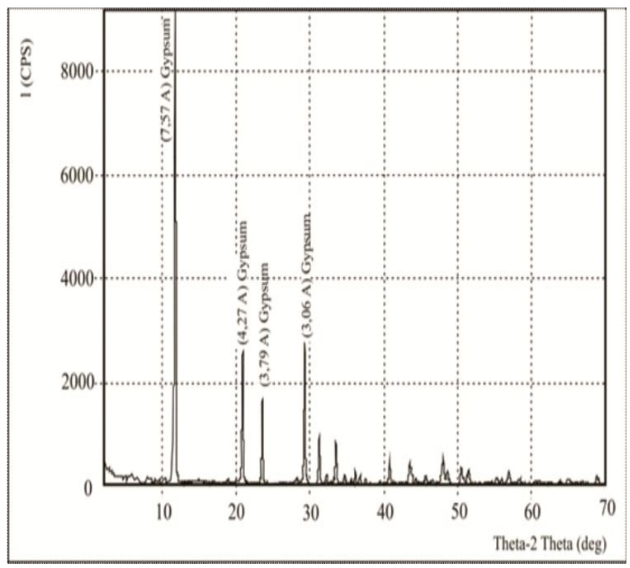

Figure 3. XRD diffractogram for the sample 4 (Orange gypsum).

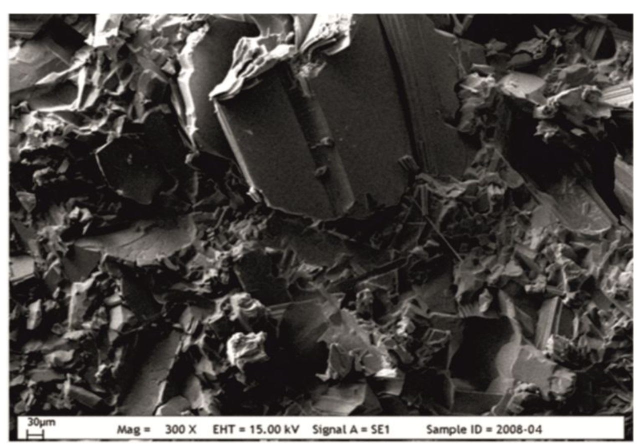

Figure 4. SEM photograph of the colored (white) massive gypsum mineral having conchoidal breaking surfaces.

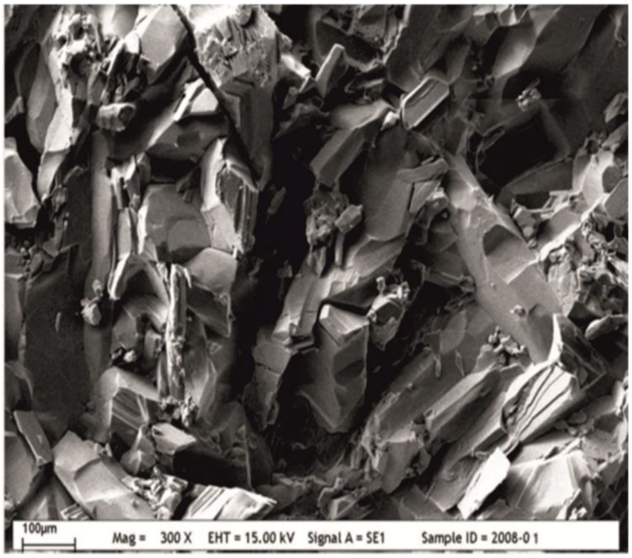

Figure 5. SEM photograph of the colored (orange) massive gypsum mineral having conchoidal breaking surfaces.