Chromatite and its Cr\(^{3+}\)- and Cr\(^{6+}\)-bearing precursor minerals from the Nabi Musa Mottled Zone complex, Judean Desert

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**ABSTRACT**

Chromatite (CaCrO\(_4\), tetragonal) is mainly known from Cr\(^{6+}\)-contaminated soils associated with chromium ore processing residue. This extremely rare mineral was found at the Nabi Musa locality (Judean Desert, Israel), in a peculiar rock complex of the Mottled Zone. We have explored the possible mechanisms responsible for leaching Cr\(^{6+}\) from natural rocks, by means of field observations, batch experiments, thermodynamic modeling, and mineralogical analyses of the Nabi Musa rocks (XRPD, EMPA, SEM, FTIR, and optical microscopy). A remarkable feature of the Mottled Zone rocks is a broad occurrence of high- and ultrahigh-temperature combustion metamorphic rocks, with Cr\(^{3+}\) accumulated mainly in opaque minerals such as Fe-spinel, brownmillerite, and perovskite. Another feature of the Mottled Zone sequence is abundant Cr\(^{3+}\) (bentorite and volkonskoite) and Cr\(^{6+}\) mineralization (Cr\(^{6+}\)-bearing ettringite and baryte-hashemite solid solution) in low-temperature hydrothermal veins. Field, mineralogical, and thermodynamic modeling data suggest that Cr was leached from Cr\(^{3+}\)-bearing opaque minerals during late hydrothermal alteration of combustion metamorphic rocks by unusual hyperalkaline waters (pH up to 12). The Cr\(^{3+}\) was then oxidized to Cr\(^{6+}\), and subsequently partially immobilized in Cr\(^{6+}\)-bearing ettringite. As a consequence of the highway construction across Nabi Musa hill in 2006, the buried veins filled by Cr\(^{6+}\)-substituted ettringite were exhumed and exposed to supergene alteration. The ensuing decomposition of Cr\(^{6+}\)-bearing ettringite was followed by Cr\(^{6+}\) release into pore waters in rainy seasons, and then by precipitation of chromatite on the evaporation barrier under the hard desert insolation in dry seasons. The chromatite formation has been due to both unique rock and water chemistry of the Mottled Zone sequence and to the arid climate of the Judean Desert.

**Keywords:** Chromatite, calcium chromate dehydrate, hexavalent chromium mineralization, Cr\(^{6+}\)-bearing ettringite, bentorite, hyperalkaline waters, Mottled Zone, Judean Desert

**INTRODUCTION**

Chromium is present in soils, minerals, and rocks mainly as Cr\(^{3+}\), whereas Cr\(^{6+}\) compounds form and very rarely remain stable under natural, near-surface conditions. Chromium can enter the environment through several natural processes, such as weathering, volcanic exhalation, or biogeochemical processes, as well as through human activities. Hexavalent Cr is relatively mobile in supergene environments. It is commonly leached by rain and thaw water from dumps and then migrates into soils and into surficial and ground waters. Reactions of Cr\(^{6+}\)-bearing solutions with soil mineral matter produce cryptocrystalline solid precipitates (chromatite, crocoite, and baryte-hashemite solid solutions) in the vicinity of Cr-bearing waste repositories (Palmer 2000; Bajda 2005). Unlike the manmade precipitates, natural chromatite (CaCrO\(_4\), tetragonal system, space group P4\(_1\)/amd) is a very rare mineral. Until recently, it was reported from a single locality of the Maale Adummim complex in the so-called Mottled Zone (MZ), the Judean Desert (Eckhardt and Heimbach 1963; Gross 1977).

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We discuss data from another chromatite locality, newly discovered in the Mottled Zone: Nabi Musa hill 5 km southeast of the Maale Adummim area (Fig. 1). Our research has focused on gaining precise information about Cr\(^{3+}\)- and Cr\(^{6+}\)-bearing minerals in the MZ complex. We attempt to infer the Cr sources and chromatite origin from the available field and analytical evidence (assemblages, chemistry, and morphology of the minerals), coupled with thermodynamic modeling.

**THE MOTTLED ZONE**

**Geology and mineralogy**

There are 15 complexes composed of peculiar rocks known as the Mottled Zone, or the Hatrurim Formation, on both sides of the Dead Sea Transform, in Israel and Jordan, within Upper Cretaceous marine, calcareous sediments (Fig. 1). The Mottled Zone (MZ) is a melange of diverse sediments (indurated chalk-like mass, marl, limestone, less abundant dolomite, chert, and phosphorite) with numerous foci of high-temperature, low-pressure combustion metamorphic (CM) rocks. All strata are densely veined and altered by late hydrothermal solutions...