

## Crystal field effects in chromium and its partitioning in the mantle

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**Abstract**— $\text{Cr}^{3+}$  ions have a strong preference for octahedral sites in mineral structures and discriminate against tetrahedral sites, whereas  $\text{Cr}^{2+}$  ions favor distorted environments, according to crystal field theory. All structure-types proposed for the transition zone and lower mantle contain six-coordinated sites, so that  $\text{Cr}^{3+}$  ions may be distributed over several phases in the Earth's interior. In the upper mantle, however, stabilization energies derived from crystal field spectra suggest that the enrichment of  $\text{Cr}^{3+}$  follows the sequence: spinel > garnet > pyroxene or olivine. High-spin  $\text{Cr}^{2+}$  ions, which may occur at very high pressures and low oxygen fugacities, are predicted to be stabilized in deformed sites of the olivine and  $\text{Sr}_2\text{PbO}_4$  structure-types. Low-spin  $\text{Cr}^{2+}$  ions may also occur in the  $\text{CaFe}_2\text{O}_4$  structure-type in the lower mantle. It is proposed that some chromite inclusions in forsterites from the upper mantle are formed by pressure-released oxidation of  $\text{Cr}^{2+}$  ions originally present in olivine or spinel modifications of  $\text{Mg}_2\text{SiO}_4$ .

### INTRODUCTION

CHROMIUM, the fourth metal in the first transition series, is a typical transition element because it has incompletely filled inner atomic orbitals (i.e.  $3d$ ) and, as a result, exists in a variety of oxidation states. Crystal field effects resulting from interactions of the bonded atoms with electrons in partially filled  $3d$  orbitals of Cr not only lead to the spectacular variety of colors characteristic of Cr compounds, but also to important fractionation processes of this element within and between minerals in the Earth. This paper discusses some aspects of crystal field theory (ORGEL, 1966; BURNS, 1970) bearing on the partitioning of chromium in phases of the mantle and crust.

### CRYSTAL FIELD ENERGIES

The electronic configuration of elemental chromium ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1 \equiv [\text{Ar}]3d^5 4s^1$ ) is such that all oxidation states from Cr(VI) to Cr(I) can occur. In terrestrial minerals in the crust, the Cr(III) and Cr(VI) states predominate as the ions  $\text{Cr}^{3+}$  ( $[\text{Ar}]3d^3$ ) and  $\text{CrO}_4^{2-}$  ( $[\text{Ar}]$ ), respectively (BURNS and BURNS, 1975). Chromate-bearing minerals are known to form by secondary alteration on the crust, but they probably play a negligible role in the fractionation of chromium in the mantle. Crystal chemical data for certain lunar minerals indicate that divalent  $\text{Cr}^{2+}$  ions ( $[\text{Ar}]3d^4$ ) may be present in phases that crystallized under low oxygen fugacities (HAGGERTY *et al.*, 1970; BOYD and SMITH, 1971). The relatively high abundances of chromium found in inclusions in diamonds from kimberlites have been attributed to the presence of  $\text{Cr}^{2+}$  ions in the olivine structure (MEYER and BOYD, 1972; SOBOLEV, 1972; PRINZ *et al.*, 1973; SUDDABY, 1973). Evidence presented later suggests that the Cr(II) state may be formed at high pressures and temperatures in the Earth's interior.

On Earth, the geochemistry and mineralogy of Cr(III) phases are dominated by the occurrence of  $\text{Cr}^{3+}$  ions in octahedral coordination only. According to crystal field theory, the five  $3d$  orbitals of first series transition metal ions are split into two energy levels when the cation is surrounded by ligands (e.g. oxygen anions). In octahedral coordination, three of the  $3d$  orbitals (the  $t_{2g}$  set) are stabilized relative to the other two (the  $e_g$  set), the energy separation (crystal field splitting) between the  $t_{2g}$  and  $e_g$  levels being denoted by  $\Delta_0$ . Each electron in a  $t_{2g}$  orbital stabilizes the cation by  $\frac{2}{5}\Delta_0$ , whereas each electron in an  $e_g$  orbital destabilizes it by  $\frac{3}{5}\Delta_0$ . The  $\text{Cr}^{3+}$  ion with three  $3d$  electrons occupying singly each  $t_{2g}$  orbital (Fig. 1) acquires a very high crystal field stabilization energy of  $\frac{9}{5}\Delta_0$  in octahedral coordination (approximately 60 kcal/g ion  $\text{Cr}^{3+}$  in oxide structures). In tetrahedral environments, the relative energies of the  $t_2$  and  $e$  orbital levels (subscript  $g$  omitted because a tetrahedron lacks an inversion center) are reversed relative to octahedral coordination, so that the third  $3d$  electron of  $\text{Cr}^{3+}$  must occupy a less stable  $t_2$  orbital (Fig. 1) and contribute a destabilization energy to tetrahedrally coordinated  $\text{Cr}^{3+}$  ions. Moreover, the tetrahedral crystal field splitting,  $\Delta_t$ , between the more stable  $e$  orbital and less stable  $t_2$  orbital levels is such that if  $\text{Cr}^{3+}$  ions were present in tetrahedral sites, the acquired CFSE,  $\frac{4}{5}\Delta_t$ , would amount to less than 30 per cent of the CFSE of octahedrally coordinated  $\text{Cr}^{3+}$  in sites with identical ligands and metal-ligand distances. Thus,  $\text{Cr}^{3+}$  ions have a high octahedral site preference energy (McCLURE, 1957) and discriminate against tetrahedral sites in geochemical media in general, and in mineral structures in particular.

The  $t_{2g}$ - $e_g$  orbital splittings of octahedrally coordinated  $\text{Cr}^{3+}$  ions depend on the type of ligand surrounding the cation, but typically lie in the range 14,000–21,000  $\text{cm}^{-1}$ , corresponding to energies in the visible region of the electromagnetic spectrum. Electron excitations between the  $t_{2g}$  and  $e_g$  orbital levels are responsible for the colors observed in Cr(III) compounds and minerals. Absorption spectral measurements enable  $\Delta_0$  and hence CFSE's to be determined. They are estimated from the position of the band at lowest energy in the absorption spectra, corresponding to the  ${}^4A_{2g} \rightarrow {}^4E_g$  transition in octahedrally coordinated  $\text{Cr}^{3+}$  ions. Spectral energies and approximate CFSE's of  $\text{Cr}^{3+}$  ions in several oxide minerals are summarized in Table 1. The data show a trend of increasing  $\Delta_0$  with decreasing metal-oxygen distance,  $R$ , in approximate compliance with the relationship:  $\Delta \propto 1/R^5$  derived for a point charge model (DRICKAMER and FRANK, 1973). Thus,  $\text{Cr}^{3+}$

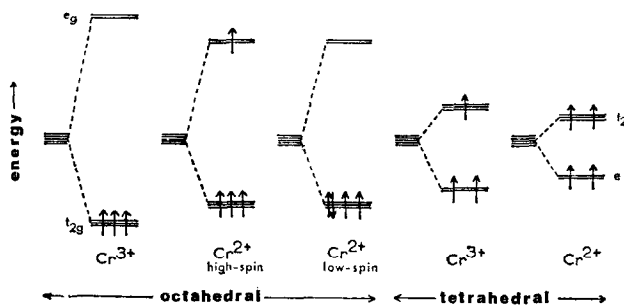


Fig. 1. Electronic configurations of chromium cations in octahedral and tetrahedral coordinations.

Table 1. Energies from Cr<sup>3+</sup> spectra

Mineral	Absorption bands (cm <sup>-1</sup> )		CFSE (kcal)	Color	Average M-O Distance (Å)	Reference
Ruby	18,200	24,900	62.5	Red	1.91	SVIRIDOV <i>et al.</i> (1973)
Spinel	18,520	24,900	63.6	Red	1.90	SVIRIDOV <i>et al.</i> (1973)
Emerald	16,130	23,530	55.5	Green	1.91	NEUHAUS (1960); POOLE (1964)
Pyrope	17,606	24,272	60.6	Red	1.905	MOORE and WHITE (1972)
Alexandrite	17,700	23,550	60.8	Red-Green	1.938	WHITE <i>et al.</i> (1967)
Uvarovite	16,191	22,676	55.7	Green	1.985	MOORE and WHITE (1972)
Ureyite	15,600	22,000	53.6	Green	1.998	WHITE <i>et al.</i> (1971); IKEDA and OHASHI (1974)
Eskolaite	16,670	21,750	57.5	Green	2.00	NEUHAUS (1960)
Kammererite	18,450	25,000	63.4	Red-Violet	2.01	NEUHAUS (1960)
Tourmaline	17,000	24,000	58.4	Green	2.05	MANNING (1969)
Epidote	16,300	24,000	56.1	Green	2.05	BURNS and STRENS (1967)
Fremolite	16,310	23,530	56.1	Green	2.07	NEUHAUS (1960)
Diopside	16,129	22,989	55.6	Green	2.08	NEUHAUS (1960)
Periclas	16,200	22,700	55.7	Green	2.109	LOW (1957)
Forsterite	16,900	23,500	58.0	Green	2.12	SCHEETZ and WHITE (1972)

acquires a higher CFSE in a 'compressed' site, such as an aluminium site, compared to a magnesium site. Note that the CFSE of Cr<sup>3+</sup> in various structure-types increases in the sequence olivine-pyroxene-garnet-spinel. Rising pressure also produces shorter interatomic distances ( $R$ ), leading to increased  $\Delta_0$  and CFSE values for Cr<sup>3+</sup> ions (DRICKAMER and FRANK, 1973). Therefore, the strong octahedral site preference of Cr<sup>3+</sup> ions should be enhanced in the mantle.

The Cr<sup>2+</sup> ion has a smaller CFSE in regular octahedral coordination (approximately 25 kcal/g ion Cr<sup>2+</sup> for oxides). This results partly from the smaller  $\Delta_0$  for divalent cations relative to trivalent ions, and partly from the destabilizing effect of the fourth 3d electron of Cr<sup>2+</sup> which occupies an  $e_g$  orbital at atmospheric pressures in oxide structures (Fig. 1). The CFSE of Cr<sup>2+</sup> is enhanced by the occurrence of the cation in distorted octahedra, whereby one of the  $e_g$  orbitals is stabilized relative to the other (the Jahn-Teller effect). As a result, Cr(II) compounds are often deformed from type-structures shown by neighboring transition metal ions (Mn<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, etc.). Conversely, Cr<sup>2+</sup> ions are predicted to be enriched in very distorted octahedral sites in mineral structures, such as the olivine M(1) site. At high pressures,  $\Delta_0$  for Cr<sup>2+</sup> may become large enough to favor the existence of low-spin Cr<sup>2+</sup> ions with all four electrons in  $t_{2g}$  orbitals (Fig. 1). Divalent Cr<sup>2+</sup> is also found in tetrahedral sites in spinels (ULMER and WHITE, 1966; GRESKOVICH and STUBICAN, 1966; MAO and BELL, 1975), where it acquires a CFSE of about 8 kcal/g ion Cr<sup>2+</sup>.

# STRUCTURE-TYPES AND ENERGY LEVELS OF MANTLE MINERALS

A variety of evidence indicates that common minerals found in the crust and upper mantle transform to denser polymorphs at high pressures towards the lower mantle (RINGWOOD, 1973). Proposed structure-types for various depths in the mantle, together with the coordination numbers of the cation sites, are contained in Fig. 3 which is discussed later. There is a general rise of coordination number of the cation sites in the denser polymorphs. Thus, the six-coordinated sites accommodating (Mg,  $\text{Fe}^{2+}$ ) in the olivine and spinel structures become 7-, 8- and 9-coordinated in the denser strontium plumbate, calcium ferrite, and potassium nickel fluoride structure-types, respectively. Recent studies (BASSETT and MING, 1972; KUMAZAWA *et al.*, 1974) suggest that post-spinel phases may disproportionate to the periclase ( $\text{MgO}$ ) and stishovite ( $\text{SiO}_2$ ) structure-types at the very high pressures and temperatures of the lower mantle. The eight-coordinate sites in pyroxenes and garnets increase to 12-fold coordination in the perovskite structure-type, whereas tetrahedrally coordinated silicon in crustal minerals would become octahedrally coordinated in the dense structure-types predicted for the lower mantle. The configurations of the oxygen coordination polyhedra in these structures, together with the relative energies of the  $3d$  orbitals of transition metal ions in the sites, are shown in Fig. 2. These data are modified from GAFFNEY (1973).

## FRACTIONATION OF CHROMIUM IN THE MANTLE

The high CFSE acquired by  $\text{Cr}^{3+}$  ions in octahedral sites, coupled with the enhanced stabilization energy obtained in a compressed site, indicate that  $\text{Cr}^{3+}$  should continue to have a high octahedral site preference energy in the lower mantle.

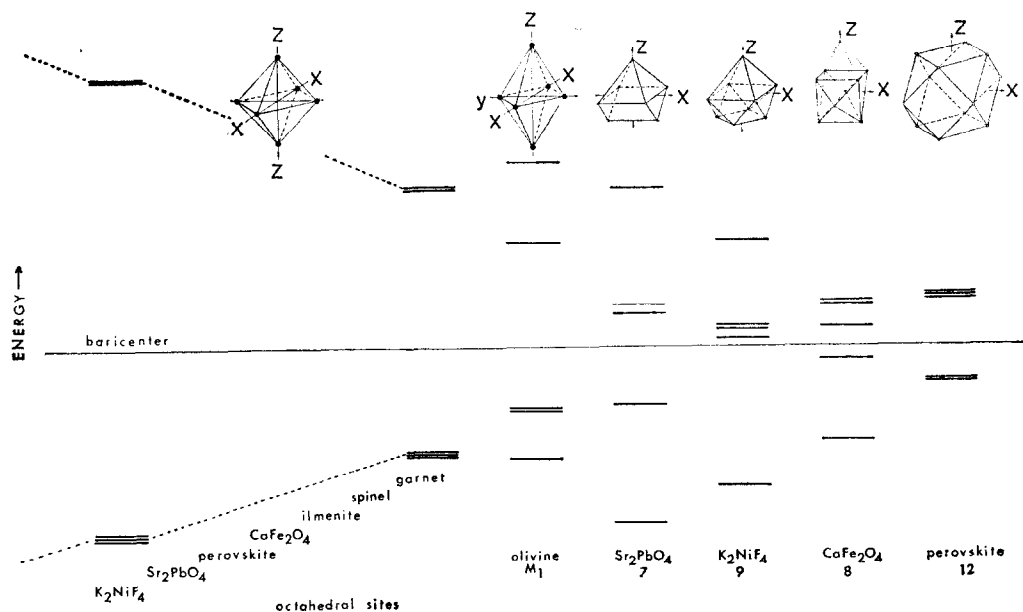
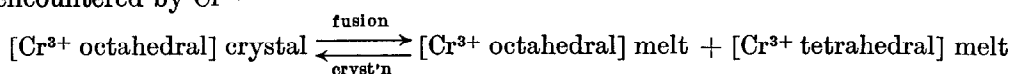


Fig. 2. Schematic energy levels of transition metal  $3d$  orbitals in coordination sites of structure-types proposed for ferromagnesian silicate phases in the mantle (based on data of GAFFNEY, 1972).

The coordination number of  $\text{Cr}^{3+}$  is unlikely to change with pressure because the radius ratio,  $\text{Cr}^{3+}/\text{O}^{2-} = 0.615 \text{ \AA}/1.40 \text{ \AA} = 0.44$ , lies near the lower limit of the range (0.414–0.732) predicted for octahedrally coordinated cations at low pressures. Although the radius ratio increases with pressure due to the greater compressibility of the highly polarizable  $\text{O}^{2-}$  ion, it is considered unlikely that higher coordination numbers will be induced for  $\text{Cr}^{3+}$  at pressures encountered in the lower mantle. Thus,  $\text{Cr}^{3+}$  ions, if they occur as such in the lower mantle, are expected to favor octahedral sites in the perovskite, ' $\text{K}_2\text{NiF}_4$ ' and ' $\text{CaFe}_2\text{O}_4$ ' (or periclase) structure-types (Fig. 3). In the transition zone,  $\text{Cr}^{3+}$  ions may be accommodated and stabilized in octahedral sites of the ' $\text{Sr}_2\text{PbO}_4$ ', ' $\text{CaFe}_2\text{O}_4$ ', ilmenite, perovskite and garnet structures. In the upper mantle,  $\text{Cr}^{3+}$  ions will be partitioned between the olivine, pyroxene, garnet and remnant spinel phases, in concentrations related to the CFSE acquired in each structure. The CFSE data summarized in Table 1 suggest that the order of  $\text{Cr}^{3+}$  enrichment in the upper mantle is:

spinel > garnet > pyroxene  $\approx$  olivine.

Note that the high octahedral site preference energy of  $\text{Cr}^{3+}$  also mitigates against high concentrations of chromium in fusion products of pyrolite. Melts formed from silicates generate an array of octahedral and tetrahedral sites, so that the equilibrium encountered by  $\text{Cr}^{3+}$



lies strongly to the left. This explains why  $\text{Cr}^{3+}$  ions are observed to be concentrated in minerals in residual lherzolites (JACKSON and WRIGHT, 1970; CARTER, 1970; BURNS, 1973).

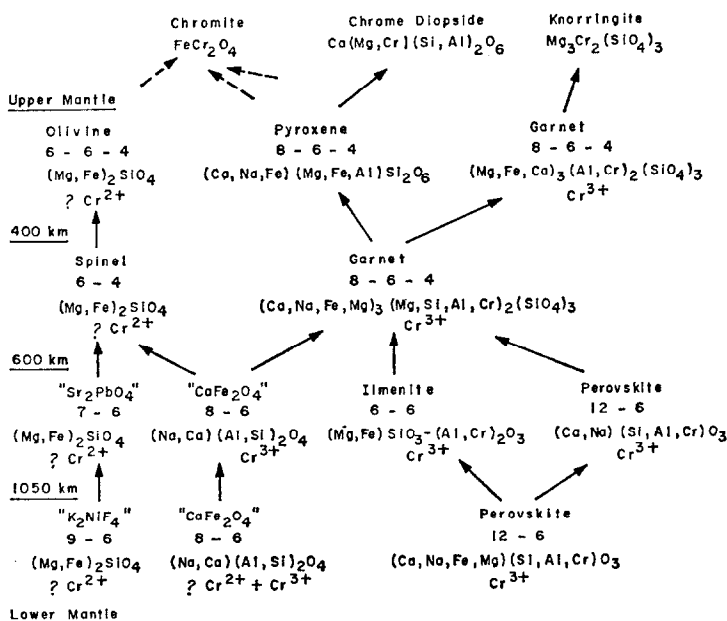


Fig. 3. Partitioning scheme for chromium in structure-types in the mantle.

In the fractionation scheme outlined in Fig. 3, it is suggested that  $\text{Cr}^{2+}$  ions also may occur in the lower mantle. They are predicted to be formed by pressure-induced reduction of  $\text{Cr}^{3+}$  ions, by analogy with processes observed in compounds and minerals containing  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Cu}^{2+}$  ions. For example, high pressure Mössbauer spectral measurements of iron (III) compounds (DRICKAMER *et al.*, 1970) and minerals (BURNS *et al.*, 1972a, b) have demonstrated that reversible reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions occurs at high pressures and temperatures, leading to the suggestion that negligible amounts of ferric iron occur in the lower mantle (BURNS *et al.*, 1972a, b; TOSSELL *et al.*, 1972). Spectral measurements have also demonstrated that reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  ions and  $\text{Cu}^{2+}$  to  $\text{Cu}^{+}$  ions occurs at high pressures (GIBBONS *et al.*, 1974; AHSBAHS *et al.*, 1974; WANG and DRICKAMER, 1973). If similar behavior occurs in chromium, the  $\text{Cr}^{2+}$  ions derived by pressure-induced reduction of  $\text{Cr}^{3+}$  would be stabilized in the distorted 7-coordinate site of the ' $\text{Sr}_2\text{PbO}_4$ ' structure-type (Fig. 2) and might occur in the low-spin state in the ' $\text{CaFe}_2\text{O}_4$ ' structure-type in the lower mantle, by analogy with low-spin  $\text{Fe}^{2+}$  (GAFFNEY, 1972).

Fractionation of  $\text{Cr}^{2+}$  in the transition zone could eventually lead to the presence of divalent chromium in olivines in the upper mantle (MEYER and BOYD, 1972; SOBOLEV, 1972), where it is predicted to be stabilized and enriched in the M(1) site of the olivine structure (BURNS, 1970). However, because most of the pressure-induced reductions of Fe(III) compounds are reversible with some hysteresis (DRICKAMER *et al.*, 1970), it is proposed that pressure-released oxidation of most of the  $\text{Cr}^{2+}$  ions to  $\text{Cr}^{3+}$  ions would occur in the upper mantle, leading to exsolution of chromite crystallites frequently observed in olivines.

The discussion has centered on chromium coordinated to oxygen in structures derived from olivine, pyroxene, garnet and spinel. Other structure-types in the mantle that may be relevant to chromium include the rutile and hollandite structures, representing dense polymorphs of silica (stishovite) and feldspars, respectively. The hollandite structure is related to rutile, and both contain octahedral sites. The existence of synthetic  $\text{Cr}^{3+}$ -rutile structure-types might also accommodate chromium in octahedral sites in the mantle. Octahedral sites also occur in periclase which may be formed by disproportionation of  $\text{Mg}_2\text{SiO}_4$ . Chromium also forms nitride and sulfide phases such as carlsbergite ( $\text{CrN}$ ), daubréelite ( $\text{FeCr}_2\text{S}_4$ ), and brezinaite ( $\text{Cr}_3\text{S}_4$ ), all found in meteorites. Carlsbergite has the rocksalt structure with metals in octahedral coordination. Thiospinels, such as daubréelite, also transform at high pressures to denser structure-types (VAUGHAN *et al.*, 1971), including a cation-defect  $\text{NiAs}$  structure (cf.  $\text{Cr}_3\text{S}_4$ ) containing chromium in octahedral sites. Thus, octahedral coordination sites favorable for the occurrence and stability of chromium are common to a variety of minerals that might occur in the mantle.

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