

On the nature of synthetic blue diopside crystals: the stabilization of tetravalent chromium

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Abstract

Chromium-rich diopside crystals, when synthesized in air at high temperature from silicate melts, are often colored a characteristic blue, instead of green as expected from the presence of Cr(III). Previous explanations for the anomalous color, in particular that synthetic blue diopside stabilized Cr(II) in the crystal structure, are rebutted. The blue color of the synthetic diopside is shown to be associated with the stabilization of a small portion of the total Cr as Cr(IV) within the diopside structure. Cr(IV) in detectable amounts is not present initially in the silicate melts, but is produced by the reduction of Cr(VI) during the crystallization. In comparison to Cr(VI), Cr(IV) can more conveniently be incorporated into the diopside structure according to two proposed mechanisms: the alleviation of the charge compensation necessary in the Cr(VI)–Si(IV) substitution by the alternate Cr(IV)–Si(IV) substitution, or the lessening of the required charge compensation by the favorable Cr(IV)–Mg(II) substitution.

Introduction

The terrestrial distribution of chromium among igneous rock phases is readily explained by the preponderance of Cr(III) in most terrestrial processes. Recently the importance of Cr(II) has been asserted in the petrogenesis of the moon (*e.g.*, Taylor, 1975; Schreiber and Haskin, 1976) and in the mineralogy of the Earth's upper mantle (*e.g.*, Meyer, 1975; Burns, 1975). However, the characteristics of Cr(II) in geochemical systems have not been rigorously investigated, although recent studies (*e.g.*, Schreiber and Haskin, 1976) have established some basic properties of Cr(II) in silicates.

Synthetic blue diopsides have been suggested to contain Cr(II) because of their blue color (Dickey *et al.*, 1971; Mao *et al.*, 1972; Ikeda and Yagi, 1972). Most terrestrial Cr-rich diopsides have a green color, indicative of Cr(III). Since synthetic blue diopsides are easily crystallized in air at high temperature from Cr-doped silicate liquids (Dickey *et al.*, 1971; Ikeda and Yagi, 1972), this mineral was thought to afford convenient direct measurements on the properties of Cr(II). Mao *et al.* (1972) compared the crystal-field absorption spectra of natural green and synthetic blue diopsides (Fig. 1), and Burns (1975) calculated the stabilization energy of Cr(II) in minerals on the basis of the spectral features of the blue diopside.

Nevertheless, the hypothesis that the blue color is imparted by Cr(II) is, at best, speculative, but has been accepted as valid (Burns and Burns, 1975) in the absence of another more compelling explanation.

Even on the basis of present knowledge, the presence of Cr(II) in synthetic blue diopside is difficult to rationalize. Blue diopside is experimentally crystallized in air from a silicate melt in which the Cr(VI)–Cr(III) redox equilibrium has been established (*e.g.*, Bamford, 1962; Nath *et al.*, 1965; Schreiber and Haskin, 1976). Extremely reducing conditions are necessary to produce appreciable quantities of Cr(II) in silicate liquids (*e.g.*, Froberg and Richter, 1968; Paul, 1974; Schreiber and Haskin, 1976). Likewise, very reducing conditions are required to synthesize blue Cr(II)–orthosilicate (Healy and Schottmiller, 1964; Scheetz and White, 1972), even though a blue forsterite which contains Cr(III) at Mg-lattice sites has also been produced in air (Finch and Clark, 1971).

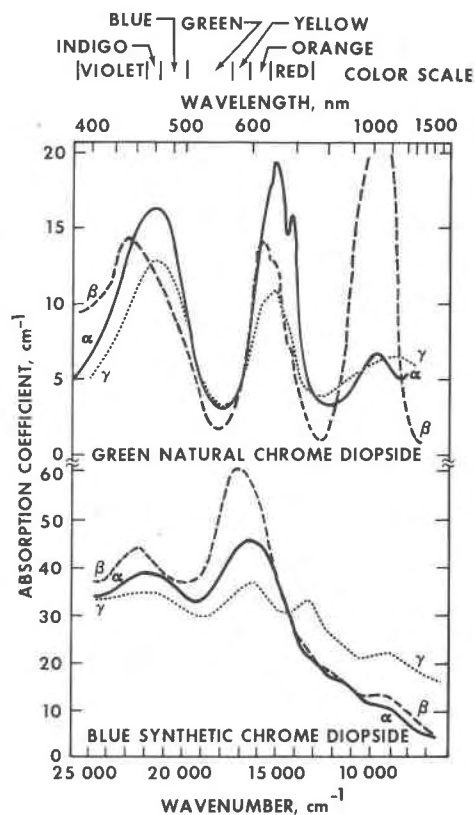
The occurrence of Cr(III) in tetrahedral lattice sites or the presence of lattice defects has also been postulated as the cause of the color of synthetic blue diopside (Dickey *et al.*, 1971; Ikeda and Yagi, 1972). Since Cr(III) readily substitutes into the favorable octahedral *M1* lattice site of diopside (*e.g.*, Burns, 1970), Cr(III) would not be expected to behave differently in the experimentally produced blue diopsides.

This paper will advance substantial experimental evidence to dispel all previous explanations for the color of blue diopside. The characteristic color will instead be attributed to the stabilization of a portion of the total Cr as Cr(IV) in diopside crystals synthesized under mildly oxidizing conditions. Although chromium exists in all valence states from 0 to +6 in inorganic compounds with a corresponding wide range of colors (*e.g.*, Poole, 1964; Cotton and Wilkinson, 1966), the presence of the Cr(III)–Cr(VI) redox pair in terrestrial systems and of the Cr(II)–Cr(III) redox pair in lunar basalts dominates the geochemical distribution of chromium (Burns and Burns, 1975). In addition Cr(0) has been found in highly reduced meteorites (Olsen *et al.*, 1973). Cr(V) has been identified as a trace component in oxidized synthetic silicate melts (*e.g.*, Garif'yanov, 1963; Schreiber and Haskin, 1976) and in geologically significant crystals (*e.g.*, Banks *et al.*, 1967; Greenblatt *et al.*, 1967; Grisafe and Hummel, 1970 a, b). The proposed existence of Cr(IV) in synthetic blue diopside will add the occurrence of yet another Cr valence state to the list of chromium species in minerals. Other claims for the stabilization of Cr(IV) in glasses (Lunkin *et al.*, 1968) and in crystals (Johansen, 1972) have previously been advanced.

Experimental methods

Homogeneous, bulk synthetic glasses with a diopside composition or a composition defined by the acronym FAD (approximately 24% forsterite, 6% anorthite, and 70% diopside by weight) were prepared from high-purity component oxides by repeated fusions, quenchings, and grindings. To each was also added 0.5 to 2 weight percent Cr₂O₃ as trace component. Sample syntheses were performed in 1-atm, high-temperature furnaces with sample atmospheres controlled by CO:CO₂ gas mixtures. Small Pt capsules holding about 200 mg of the initial glass powder served as sample containers. Temperatures were measured by a Pt/Pt90Rh10 thermocouple immediately adjacent to the charge; oxygen partial pressures were determined from fixed CO:CO₂ gas-flow ratios calibrated by a ceramic electrode assembly (Schreiber and Haskin, 1976).

Experimental silicate glasses of diopside or FAD composition were synthesized by melting at the desired conditions above the liquidus. Synthetic diopside crystals were grown at the desired oxygen partial pressure by remelting the initial powder above the liquidus followed by isothermal crystallization at about 1350°C. For composition FAD, the diopside



ADAPTED FROM MAO *et al.* (1972)

Fig. 1. Crystal field absorption spectra of green natural Cr-diopside and blue synthetic Cr-diopside as measured in the three polarization directions by Mao *et al.* (1972). The peak at 10000 cm⁻¹ in the natural diopside is due to the presence of iron.

coexisted with forsterite and quenched liquid. Samples were also prepared by isothermal devitrification of the initial glasses.

Indirect chemical redox titrations were used to determine the fraction of each chromium valence state in the synthetic glasses and crystals. The procedure was a modification of the basic design of Close and Tillman (1969) and is described in detail by Schreiber (1976). Unfortunately, the exact valence state of Cr can only be inferred by this method. If the Cr redox pair is known, however, the titration in conjunction with a total Cr analysis provides a quantitative estimate of the concentration of each Cr valence species.

Electron paramagnetic resonance (EPR) spectra of the samples were recorded at X-band and ambient temperature under constant sample configuration. 20.0 ± 0.1 mg aliquots of the finely powdered glasses or crystals were used as samples in matched 3 mm ID Suprasil quartz tubes. The EPR measurements were used for quantitative estimates of the Cr(III) content

of the glasses (Schreiber and Haskin, 1976), for identification of other Cr valence states in the glasses and crystals (O'Reilly and MacIver, 1962), and for determination of structural sites in which the Cr ions are located.

Results and discussion

Experiments in which diopside crystals were grown from silicate liquids as a function of the oxygen partial pressure clearly indicated the inadequacies of previous explanations concerning the nature of synthetic blue diopside. For both melt compositions, blue diopside crystallized only under an oxygen partial pressure approximating that of air. If the synthetic diopside crystallized at an oxygen partial pressure of 10^{-3} to 10^{-8} atm at 1350°C , it always had a green color. Devitrification experiments gave analogous results.

These experiments show that the color of blue diopside must be related to the redox state of Cr and not to simple changes in the substituted lattice sites, since the incorporation of Cr(III) into a particular diopside lattice site is probably not dependent upon the oxygen partial pressure during synthesis. The premise for the stabilization of Cr(II) within blue diopside is, however, directly contrary to the experimental results, since the blue color is accentuated at the high oxygen partial pressures and not the low. Consequently, the only plausible explanation for the blue color is the presence of a Cr valence state greater than Cr(III).

The silicate liquid from which blue diopside crystallizes is yellowish-green and contains about 10–20 percent (the actual fraction depends upon temperature and composition) of the total Cr as Cr(VI) with the remainder as Cr(III). At an oxygen partial pressure of about 10^{-3} atm, the quenched melt contains mostly Cr(III) and is dark green, whereas at lower oxygen partial pressures the glasses become progressively more blueish with the formation of an appreciable fraction of Cr(II) in the silicate liquid. However, even from a silicate melt whose Cr content is proportionately 30 percent Cr(II) and 70 percent Cr(III) at an oxygen partial pressure of 10^{-8} atm, the crystallized diopside is still green. The distribution coefficient of Cr(III) between diopside and melt is about 3 times that of Cr(II), so that diopside concentrates Cr(III) relative to Cr(II) (Schreiber and Haskin, 1976). Cr-rich diopside has also been produced experimentally under a variety of mildly reducing conditions, always resulting in green diopside (*e.g.*, Seward, 1971; Ikeda and Yagi, 1972; Duke, 1976).

Not surprisingly, redox titrations on the synthetic diopsides indicate that green diopside grown at an oxygen partial pressure of 10^{-3} atm contains only Cr(III), whereas blue diopside crystallized in air contains Cr of a higher valence state in addition to the Cr(III).

The experimental EPR spectra of synthetic green and synthetic blue diopsides of comparable total Cr content are shown in Figure 2A and B. The Cr(III) resonance fine structure at the approximate magnetic field of 1500 gauss [$g_{\text{eff}} \sim 5$] is identical for both crystals, indicative of Cr(III) in the *M1* octahedral lattice site in each crystal of different color. The strong, symmetric peak at $H \sim 3400$ gauss [$g_{\text{eff}} = 1.98$] which appears in this particular green diopside's spectrum can be attributed to an insignificant amount of Cr(III)–Cr(III) exchange coupled pairs (*e.g.*, Fournier *et al.*, 1971) associated with the higher Cr(III) concentration in that diopside. When synthesized under conditions which dictated lower Cr(III) concentrations, the green diopside would produce an EPR spectrum without the broad Cr(III)–Cr(III) resonance and which was virtually identical to the blue diopside's spectrum.

The EPR spectra of representative Cr-doped silicate melts (glasses) are shown in Figure 2C through F; assignments of the Cr resonances in the spectra are according to the work of Schreiber (1976). An EPR spectrum of a silicate melt from which blue diopside would crystallize is given in Figure 2C and illustrates the presence of trace amounts of Cr(V) ions in the melt by the strong asymmetric resonance at $H \sim 3400$ gauss, in addition to the presence of Cr(III) ions by the peak at $H \sim 1400$ gauss. The strong Cr(V) band occurs only in the EPR spectra of glasses synthesized in air or more oxidizing atmospheres, the same conditions under which blue diopside is produced. However, the EPR spectrum of synthetic blue diopside does not show any peak attributable to Cr(V); thus the blue diopside crystals must effectively exclude the traces of Cr(V) present in the initial liquid. An EPR spectrum of a silicate melt from which green diopside precipitates is given in Figure 2D. The broad, intense band is once again assigned to spin–spin exchange coupling of Cr(III) pairs which occur only above a certain critical Cr(III) concentration (this critical concentration is variable and quite sensitive to bulk melt composition and temperature). Green diopside can also be crystallized from a silicate melt containing less Cr(III), whose EPR spectrum would appear as illustrated in Figure 2F. The EPR spectral pattern of green diopside crystals with respect to the absence

or presence of the Cr(III)–Cr(III) resonance roughly reflects the pattern of the corresponding glass and, thus, just the absolute Cr(III) concentration. Even though the Cr(V) and Cr(III)–Cr(III) resonances dominate the EPR spectra when they occur, studies (e.g., Schreiber, 1976) have shown that the relative concentrations of these species are insignificant with respect to Cr(VI), isolated Cr(III), and Cr(II) in the melts. The artifact of a resonance indicated in Figure 2F at $H \sim 3400$ gauss is always observed in Cr-doped glasses, and is possibly caused by very small amounts of Cr(V) or by Cr(III) in axially-distorted octahedral coordination (Paul and Upreti, 1975).

The properties of Cr(VI) in silicate melts have been previously investigated; Cr(VI) exists in tetrahedral coordination as discrete chromate, CrO_4^{2-} , groups and imparts a yellow color to glasses even at low concentration, as a consequence of the absorption edge of an intense near-UV absorption band (e.g., Bamford, 1962; Nath *et al.*, 1965). Since Cr(VI) is present in the silicate liquid from which blue diopside crystallizes, Cr(VI) is also expected in the crystals. However, if Cr(VI) incorporates as chromate or dichromate groups within the diopside crystals, the crystals should be colored yellow-green, similar to the glass. It is inconceivable that the presence of Cr(VI) with its associated intense near-UV absorption would shift the Cr(III) transmission band to a shorter wavelength in the progression from green to blue diopside (Fig. 1); instead the shift would be to a longer wavelength.

Despite the inferred absence of measurable amounts of Cr(IV) in silicate glasses for all synthesis conditions studied to date (Schreiber, 1976), the conclusion that the anomalous color of blue diopside is due to the stabilization of Cr(IV) in the crystal structure is justified by comparison to work of others and is implied from experimental evidence.

Lunkin *et al.* (1968) claim to have stabilized Cr(IV) in an aluminosilicate glass under weakly oxidizing conditions. Johansen (1972) argued for the existence of Cr(IV) in blue Ca_3SiO_5 crystals under appropriate synthesis conditions, on the basis of EPR and reflectance spectra. A reinterpretation of the chemical analyses and optical spectra of blue Ca_3SiO_5 crystals reported by Boikova *et al.* (1966) is also consistent with the stabilization of Cr(IV) within this crystal lattice. Both Lunkin *et al.* (1968) and Johansen (1972) indicate that their resulting optical spectra are consistent with the presence of Cr(IV) in the silicates. Indeed, a comparison of these spectra with that of synthetic blue diopside shows a surprising similarity of spectral features (Fig. 3) for the different host

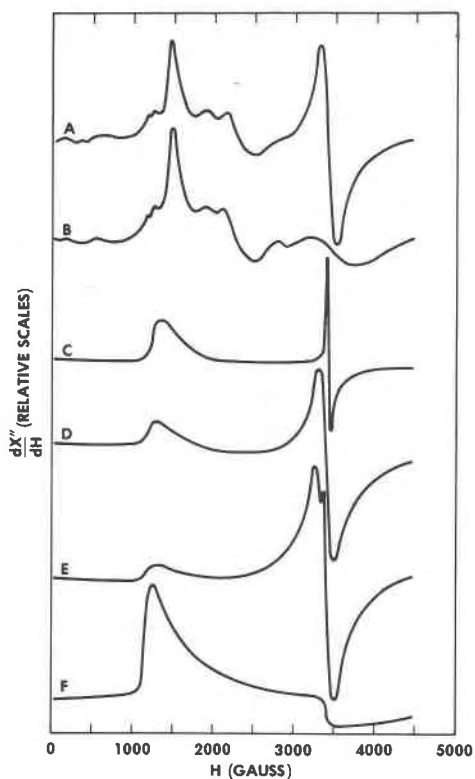


Fig. 2. EPR spectra of representative Cr-doped diopside crystals and glasses. All EPR spectra were measured at X-band ($\nu = 9.53$ GHz). The derivative scale plotted in the y direction is relative for each individual spectrum; the intensities compared among spectra do not indicate relative concentrations from one sample to another. The resonances at $H \sim 1400$ gauss are assigned to isolated Cr(III) ions in near-octahedral coordination; the sharp, intense, asymmetric band at $H \sim 3400$ gauss is attributed to a small amount of Cr(V) ions in near-octahedral coordination; and the broad, intense, symmetric peak at $H \sim 3400$ gauss is caused by a negligible concentration of Cr(III)–Cr(III) exchange-coupled ion pairs. A: synthetic green diopside crystallized from a melt at $P(\text{O}_2) = 10^{-3}$ atm with relatively high Cr content. B: synthetic blue diopside crystallized from an identical melt in air. C: typical melt from which blue diopside would precipitate in air. D: typical melt from which green diopside would precipitate at $P(\text{O}_2) = 10^{-3}$ atm with relatively high Cr content. E: atypical melt, synthesized in air and of high Cr content, demonstrating the Cr(V) and Cr(III)–Cr(III) resonances are distinct. F: typical melt from which green diopside would precipitate, $P(\text{O}_2) = 10^{-3}$ atm or lower with relatively low Cr content.

structures. Hoskins and Soffer (1964) also present evidence for the existence of Cr(IV) in crystals of $\alpha\text{-Al}_2\text{O}_3$ grown under conditions which supposedly favored the stabilization of Cr(IV) in that lattice. However, none of these previous authors have individually made a definitive case for their arguments.

In the production of blue diopside by devitrification of Cr-rich glass in air, Dickey *et al.* (1971) no-

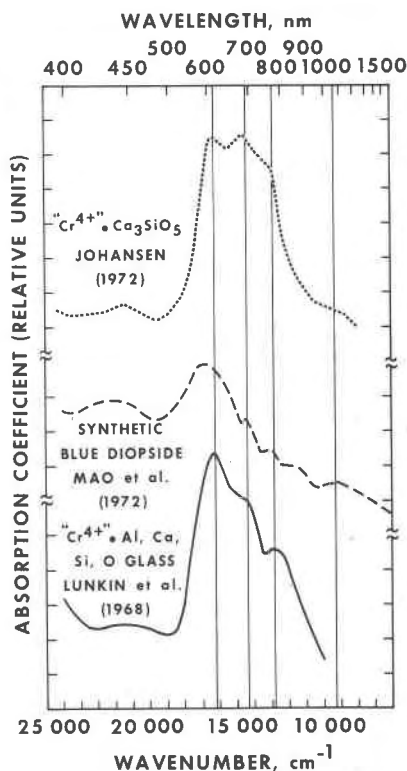


Fig. 3. Comparison of the optical absorption spectra of Cr(IV) in glass, Cr(IV) in Ca_3SiO_6 , and synthetic blue diopside. Cr(IV) should show three absorption bands; the transition at 9500 cm^{-1} may be the result of Fe contamination, while the peak at 22000 cm^{-1} is associated with Cr(III).

ticed that the resulting charge was very vesicular, as if a gas phase had been liberated in the crystallization process. This observation was confirmed in the present study. Whereas Dickey *et al.* (1971) interpreted this observation as the release of oxygen in the reduction of Cr(III) to Cr(II) during the crystallization, the vesicular samples probably suggest the evolution of oxygen as a result of the reduction of Cr(VI) to Cr(IV) in the crystallization of blue diopside.

Although CrO_4^{2-} groups exist harmoniously within a diopside liquid, a mechanism for charge compensation must operate for Cr(VI) as CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ to substitute for $\text{Si}_2\text{O}_6^{4-}$ in diopside crystals. In the synthetic systems investigated, the difference in charges can be alleviated by the unfavorable mechanism of forming silicon lattice vacancies (*e.g.*, McIntire, 1963). The substitution of CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ units [*i.e.*, Cr(IV)] into diopside would not require charge compensation. Although the ionic radius of Cr(IV) in tetrahedral coordination is about $1\frac{1}{2}$ times that of Si(IV) (Whittaker and Muntus, 1970), the size is not expected to be large enough to prevent the sub-

stitution. Alkaline-earth Cr(IV) chromates, $M_2\text{CrO}_4$, are relatively stable blue-black compounds (Cotton and Wilkinson, 1966), and PbCrO_3 can be synthesized at high pressure (DeVries and Roth, 1968). Likewise, this convenient substitution-charge compensation mechanism is consistent with the production of blue forsterite (Finch and Clark, 1971) by processes similar to that for blue diopside.

Alternatively Cr(IV) may substitute in the octahedral Mg lattice sites of diopside. The expected high octahedral site preference energy of the Cr(IV) ion (*e.g.*, Burns, 1970) might favor this explanation. Although a charge-compensation mechanism must be introduced to account for the charge disparity between Cr(IV) and Mg(II), this particular substitution would require cation vacancies which are energetically more favorable than the silicon vacancies introduced by the Cr(VI)-Si(IV) substitution. The ionic radius of Cr(IV) in octahedral coordination is somewhat smaller than that of Mg(II). However, if the octahedral site substitution of Cr(IV) is favored over the previous mechanism, it is difficult to explain why Cr(VI) is not instead reduced to the more compatible and stable Cr(III) at this site.

A choice between the two proposed mechanisms cannot be made on the basis of the present experimentation. Regardless of which mechanism is actually correct, the stabilization of Cr(IV) in the blue diopside structure is easily rationalized. Only a portion of the Cr in the synthetic blue diopside is Cr(IV); most of the Cr in the crystal is still Cr(III) as indicated by EPR, optical absorption, and redox titration. Probably no more than the amount of Cr initially present as Cr(VI) in the liquid (about 10–20% of the total Cr) is transformed into Cr(IV). However, this proportion of Cr(IV) is sufficient to shift the Cr(III) transmission band and create the observed blue hue.

Summary

Diopside, when crystallized from a melt containing Cr(VI) in addition to Cr(III), will cause the preferential reduction of Cr(VI) to Cr(IV) to afford ready substitution of Cr(IV) into the crystal lattice. The diopside crystals cannot incorporate Cr(VI) directly into the structure in the synthetic systems because of charge compensation limitations. Experimental methods of preparation, chemical and instrumental analyses, and comparisons to other studies are all consistent with this assignment. The stabilization of Cr in the uncommon +4 valence state in blue diopside crystals illustrates the powerful role that the

crystallizing lattice may exert upon the distribution of trace elements.

Acknowledgments

I thank H. V. Lauer for many discussions on the collection and interpretation of the data, L. A. Haskin for helpful comments, an anonymous reviewer whose constructive criticism added much to the paper, and C. Hartless in manuscript preparation. This work was performed in conjunction with NASA contract NAS 9-13686. The experimental research presented in this paper was accomplished while the author was at NASA Johnson Space Center, Houston, Texas, and while he was affiliated with the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

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Manuscript received, May 4, 1976; accepted for publication, December 23, 1976.