Effect of the W:Mo ratio on the shift of excitation and emission spectra in the scheelite-powellite series

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ABSTRACT

Measurement of luminescence of 21 synthetic members of the scheelite-powellite solid-solution series shows that for excitation at 250 nm, the emission peaks change from 425 nm for pure scheelite to 530 nm with the addition of 10 mol% $CaMoO_4$. From 10 to 100 mol% $CaMoO_4$, the emission peak remains at 530 nm. This emission shift is similar to that noted by previous workers who interpreted the emission shift to be the result of a single peak whose wavelength shifts regularly with a change in composition from one end member to the other. Our data, however, indicate that there are two separate peaks—a scheelite peak and a powellite peak—that combine to form a composite emission peak. The wavelength shift of the composite emission peak results from variations in the relative intensities of the scheelite and powellite peaks. The scheelite peak exhibits a marked decrease in intensity with the addition of as little as 0.2 mol% $CaMoO_4$. This decrease is not the result of Mo simply diluting the effect of W but instead appears to reflect nonradiative energy transfer from tungstate to molybdate orbitals.

The intensity of solar-stimulated luminescence increases as the Mo content in Mo-bearing scheelite increases. With as little as 8 mol% $CaMoO_4$ in the crystal, scheelite should luminesce with sufficient intensity to be detectable with a Fraunhofer line discriminator, an airborne optical instrument that detects luminescing materials.

INTRODUCTION

The fluorescence of scheelite has been known and used as a diagnostic property for the identification of this mineral since the work of VanHorn (1930). Pure scheelite fluoresces with a blue light (425 nm), but the addition of Mo, which exhibits complete solid solution with W in scheelite, results in the emission of longer-wavelength light (530 nm). The change in color has been used to approximate the amount of Mo present in a particular specimen of scheelite (Greenwood, 1943; Cannon and Murata, 1944; Shoji and Sasaki, 1978).

This study was undertaken to acquire spectral measurements of synthetic members in the scheelite-powellite ($CaWO_4$-$CaMoO_4$) solid-solution series, to determine the cause(s) of the shift of emission wavelength as the Mo content in these phosphors is increased, and to determine whether the luminescence of natural scheelite-powellite exposures could be stimulated by the Sun and detected by the Fraunhofer line-depth remote sensing method (Hemphill et al., 1983a, 1983b). The excitation of scheelite occurs dominantly at wavelengths less than 300 nm

(Grasser et al., 1982). As a result, pure scheelite cannot be excited by sunlight because no solar radiation at wavelengths shorter than 300 nm reaches the Earth's surface (Luckiesh, 1946, p. 44–48). The question of whether the addition of Mo would increase the excitation wavelength of scheelite to wavelengths greater than 300 nm has significant importance regarding the use of remote-sensing devices, such as the Fraunhofer line discriminator (FLD), which rely on the Sun as an excitation source.

Luminescence of scheelite is an intrinsic property; it is not caused by trace elements nor by defects in the crystal structure (Grasser et al., 1982). The effect on luminescence of the addition of small amounts of Mo to scheelite has been investigated by Cannon and Murata (1944), Kroger (1948), Kononov (1967), and Shoji and Sasaki (1978). These studies noted that the fluorescent color of scheelite changes from its characteristic blue to yellow with the addition of small amounts of Mo (less than 20 mol% $CaMoO_4$). Different values, however, have been reported for the wavelengths emitted by pure scheelite (418–466 nm), pure powellite (485–535 nm), and the amount of Mo necessary (10–20 mol% $CaMoO_4$) to effect the change in color (Table 1). The causes of this shift in the emission wavelengths of the scheelite-powellite solid-solution series also have not been definitively established. Most investigators imply that Mo is present homogeneously throughout the scheelite structure and that there is a single emission peak that shifts in response to the change in chemistry. Kononov (1967) alluded to the for-

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TABLE 1. Comparison of investigations of the spectral shift in the scheelite-powellite solid solution

Investigator	W color	Mo color	Appearance of 1st Mo color (mol% CaMoO₄)
Cannon and Murata (1944)	blue	yellow	14
Kroger (1948)	420 nm	535 nm	20
Kononov (1967)	466 nm	516 nm	17
Shoji and Sasaki (1978)	418 nm	485 nm	10
This paper	425 nm	530 nm	10

mation of Mo-rich regions in the scheelite structure that cause the occurrence of the yellow emission. We believe that Mo is distributed homogeneously throughout the crystal, that the emission peak results from the addition of characteristic scheelite and powellite emissions, and that the shift in the composite emission peak reflects changes in the relative intensities of the scheelite and powellite emissions as the chemistry of the mineral is changed.

METHODS

Scheelite-powellite synthesis

Twenty-one members of the scheelite-powellite solid-solution series were synthesized; their compositions are 0.0, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60, 80, 90, 95, and 100 mol% CaMoO₄. A method of directly precipitating Mo-bearing scheelite of the desired composition was adapted from a technique described by Shoji and Sasaki (1978).

$Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were weighed in appropriate proportions to provide the desired intermediate member of the solid solution. These two reagents were dissolved together in 100 mL of distilled water and slowly poured into one L of boiling distilled water containing 100 g of $CaCl_2$. The precipitate, which has the same W:Mo molar ratio as the $NaWO_4 \cdot 2H_2O$-$NaMoO_4 \cdot 2H_2O$ solution (Shoji and Sasaki, 1978), was filtered and washed in deionized water prior to drying for 24 h at 100 °C. Analysis of the products by X-ray diffraction ensured that only members of the scheelite-powellite series were present; no other phases were detected in any of the samples.

The initial products were analyzed using a fluorescence spectrophotometer (Fig. 1) as described below. Although the wavelength of the emission peaks varied with the change in composition (Fig. 2) as had previously been reported (Kroger, 1948; Kononov, 1967; Shoji and Sasaki, 1978), the luminescence intensities of individual samples were variable when compared to the intensities exhibited by samples of neighboring compositions. The diverse nature of the peak luminescence intensities may be attributed to the variable size of the crystallites. Kotera et al. (1981) and Inagaki et al. (1983) demonstrated that luminescence intensity decreases as the diameter of the crystals decreases. These changes in crystal size and luminescence intensity may be attributed to inconsistencies in the synthesis technique. Changes such as intensity and duration of agitation, rate of seed formation, particle growth of all chemical phases, rate of addition of components, the sequence in which components are added, and the aggregate size of the surface area of the particles (ideally particles of all phases would be very fine and of the same size) may enhance or reduce the quantum efficiency of a phosphor (Froelich, 1948). Leverenz (1950, p. 73) noted that the results of several investigators commonly differ widely due to idiosyncrasies of technique, even where the same ingredients and facilities are used. In order to increase the size of the crystals and their intensity, all samples were annealed in air for 96 h, similar to the procedure described by Inagaki et al. (1983). A temperature of 700 °C, near the highest temperature at which $(MoO_4)^{2-}$ is stable and will not preferentially volatilize (L. L. Y. Chang, oral comm., 1984), was used. Spectral measurements on these annealed specimens exhibited a more regular variation in their luminescence intensities (Fig. 3).
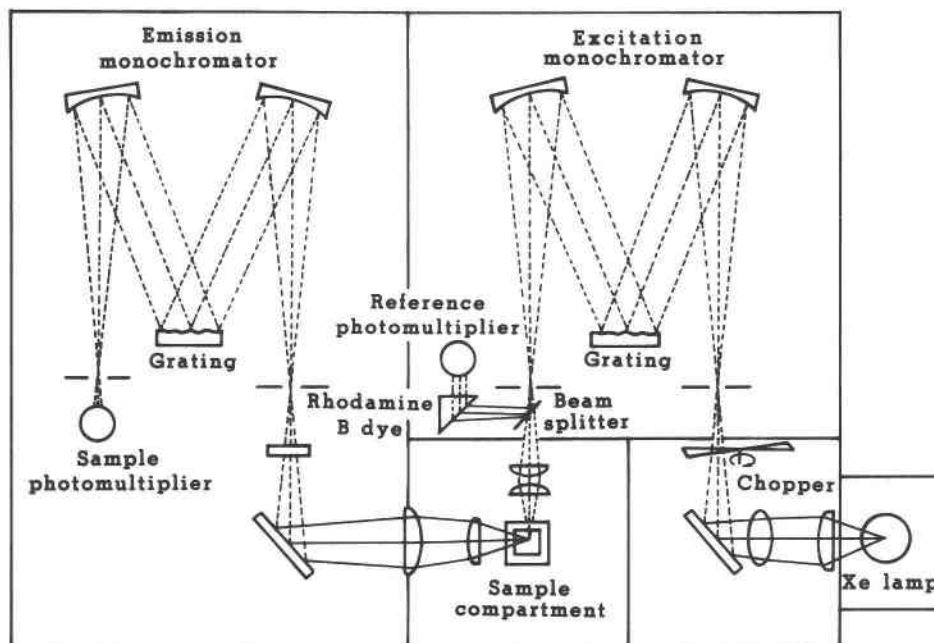

Fig. 1. Optical-path diagram of the MPF-44B fluorescence spectrophotometer (modified from Perkin-Elmer Corporation, 1978).

Annealing also introduced some random, though less pronounced, effects on intensity. Our synthetic Mo-bearing scheelites were annealed in batches containing as many as 16 samples, some of which deviated from the intensity trend established by most of the samples heated in the same batch. The deviations may have been a result of unequal heating due to heterogeneities of temperature in the oven.

Spectral measurements

Spectral measurements were made using a Perkin-Elmer MPF-44B fluorescence spectrophotometer (Fig. 1).[4] Modifications were made to the spectrophotometer after delivery to improve the quality of spectral data collected with it. A holographic grating (1200 grooves per millimeter) was installed in the excitation monochromer, thereby reducing or negating many of the random or periodic errors that had occurred while using the ruled grating delivered with the instrument. A ruled grating, 1200 grooves per millimeter and blazed at 500 nm, was installed in the emission monochromer, and improved spectral response in the infrared to wavelengths as long as 830 nm. Additional filter holders were also installed in the sample compartment so that selected blocking filters could be introduced during midscan to reduce stray light, which is especially troublesome when measuring rock and mineral powders.

Raw spectral data was modified by the corrected-spectra unit (CSU), a microcomputer that after calibration, removes the spectral features characteristic of the Xe source, monochromer optics, and the detector. Calibration of the Xe source and excitation monochromer for the wavelength region from 240 to 600 nm was achieved by using the known luminescence of an optically dense solution of rhodamine B dye in ethylene glycol. For subsequent excitation scans on samples, the information, which was stored in memory at 0.2-nm increments during the calibration run, can be recalled and used to correct the spectral scan. Calibration of the emission monochromer and detector was achieved using a standard W source and scanning from 400 to 830 nm. These correction values are stored in memory and recalled during subsequent runs on samples.

SCHEELITE LUMINESCENCE

Emission spectra

Emission spectra for each of the synthetic members of the scheelite-powellite series were measured at room temperature by using an excitation wavelength of 250 nm. The data are presented graphically in Figure 2 and are tabulated with analogous data from Shoji and Sasaki (1978) in Table 2.

Pure scheelite and pure powellite have peak emissions at 425 and 530 nm, respectively, when excited at 250 nm. Spectral shift occurs in the 0–10 mol% $CaMoO_4$ range where the peak emission shifts from 425 to 530 nm (Fig. 3). At 10 mol% $CaMoO_4$, the emission peak curve exhibits a major inflection. Above 10 mol% $CaMoO_4$, the emission peak exhibits wavelengths of approximately 530 nm. The relative intensity exhibits a minimum at 20 mol% $CaMoO_4$. The highest intensities are exhibited by pure scheelite and near pure powellite (Fig. 3).
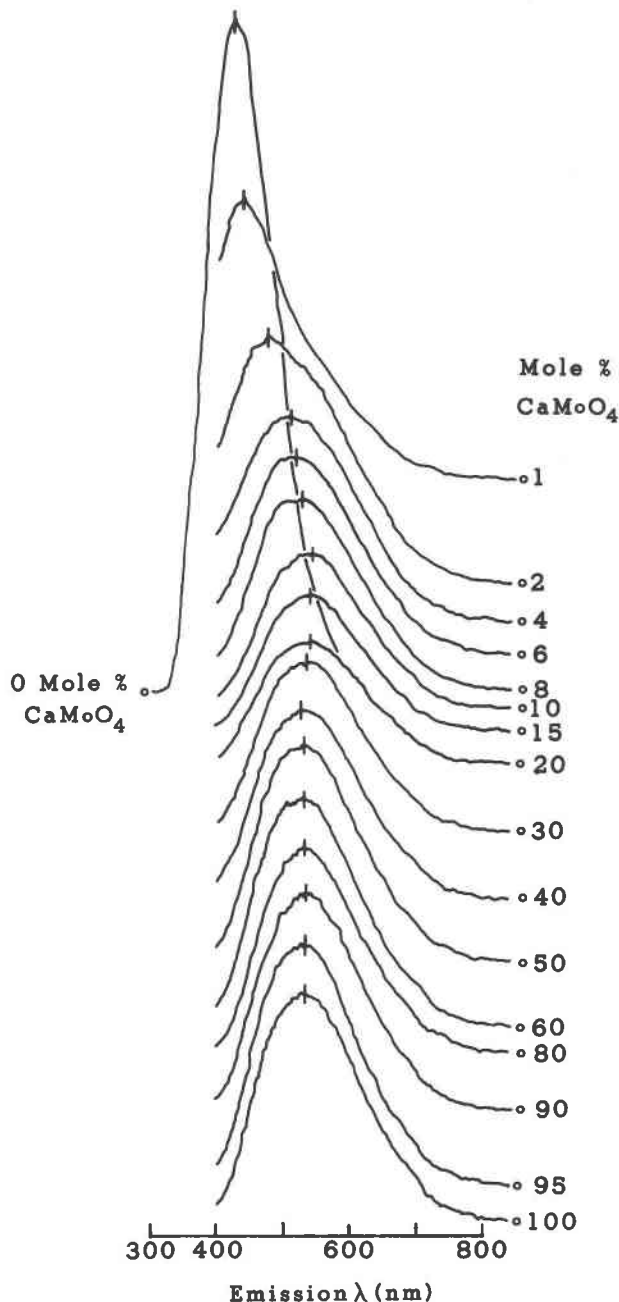
Fig. 2. Emission peaks of 17 synthetic scheelite-powellite specimens. Excitation used was 250 nm.

These data agree fairly well with descriptive results (blue, bluish white, etc.) reported by Shoji and Sasaki (1978) for synthetic scheelite-powellite phosphors. Their spectra at 0 mol% $CaMoO_4$ show a peak interpreted (by us) to be at 418 nm, which is close to our measurement of the emission peak (425 nm) for the same composition. Their peak at 100 mol% $CaMoO_4$ is interpreted to be at 485 nm, 45 nm less than our peak at 530 nm (Table 2). This discrepancy may be due to Shoji and Sasaki's data
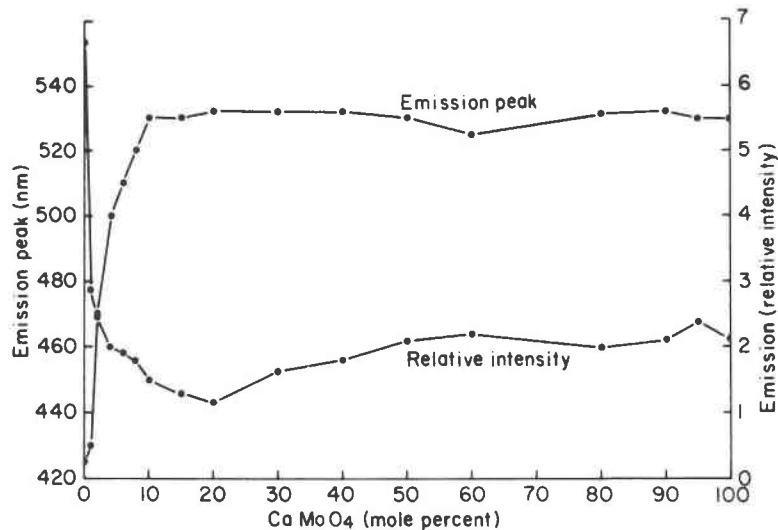
Fig. 3.   Wavelength and relative intensity of emission peak related to composition (expressed in mol% CaMoO₄) for 17 synthetic scheelite-powellite specimens. Excitation at 250 nm.

not being corrected for the spectral response of their R-374 photomultiplier detector.

Our data agree very well with the spectra of synthetic scheelite-powellite phosphors produced by Kroger (1948, p. 134–135) who showed peaks near 420 and 535 nm for 0 and 100 mol% CaMoO₄ (Table 1), respectively. Kroger (1948, p. 134) noted an inflection at 410 nm and a peak at 510 nm for the 1 mol% CaMoO₄ emission curve, neither of which was observed by us. Kroger (1948, p. 108) synthesized his samples by annealing solid reagents, and this particular sample may not have attained equilibrium or a stoichiometric distribution of Mo and W throughout the crystal structure. Our technique of directly precipitating phases with the desired compositions should have

permitted a closer approximation to equilibrium (Leverenz, 1950, p. 50) and a more accurate determination of the emission spectra.

Our data, however, are in marked contrast with Kononov's (1967) analyses of the spectra of eight natural scheelite-powellite samples that had compositions ranging from 0.12 to 16.81 mol% CaMoO₄. He observed no emission peaks shorter than 466 nm nor any longer than 516 nm. He interpreted the major peak shift to be in the four specimens that exhibited only 1.62 mol% CaMoO₄ or less. It is possible that Kononov's results were adversely affected by his apparatus in that his spectrophotometer apparently produced only uncorrected spectra (Kononov, 1967). His peak of longest wavelength, 516 nm, may actually be at a somewhat longer wavelength when measured in a corrected-spectra mode. The absence of peaks shorter than 466 nm in his data may be due to his use of a blocking filter to avoid an unwanted Hg line at 436.5 nm (sic; actually 435.8 nm; he apparently used the 253.7-nm Hg line as his primary excitation source).

Perspective plots

Luminescence of Mo-bearing scheelites is more complicated than is revealed by the emission spectra generated from one excitation wavelength, because as the excitation wavelength is varied, the wavelength of the emission peak changes (Fig. 4). One way of showing the effects of the excitation wavelength on the resulting emission is by the use of three-dimensional perspective plots, which graphically represent the luminescence of a sample. A three-dimensional perspective plot of visible and near-visible excitation and emission properties of a sample material (e.g., Fig. 5) can be made by scanning the emission monochromator out to 830 nm while the excitation monochromator is stepped at 10-nm increments beginning at 300 nm and ending 31 scans later at 600

TABLE 2.   Emission peaks scheelite-powellite (excitation at 250 nm)

Mol% CaMoO₄	Emission peaks (nm)	
	This study*	Shoji and Sasaki**
0	425	418
1	430	412
2	470	431
4	500	454
6	510	468
8	520	n.d.
10	530	474
15	530	n.d.
20	532	474
30	532	n.d.
40	532	476
50	530	n.d.
60	525	500
80	531	476
90	532	n.d.
95	530	n.d.
100	530	485

* Selection of emission peak is based upon 6 to 10 emission scan runs.
** Shoji and Sasaki (1978, p. 399). The peaks are our measurements of their emission plots; n.d. = no data as Shoji and Sasaki (1978) did not synthesize these compositions.
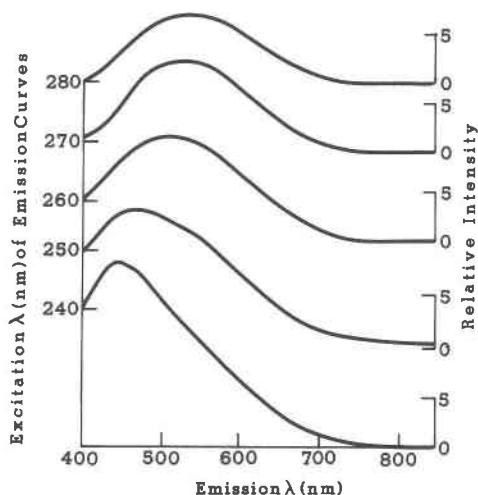
Fig. 4. Emission spectra of a scheelite-powellite specimen containing 2 mol% $CaMoO_4$ for various excitation wavelengths. Note the change in wavelength of the peak emission from 435 to 530 nm as the excitation wavelength is increased from 240 to 280 nm.

nm. The procedure is described in Theisen and Hemphill (1985).

Plots of 11 of the synthetic specimens are shown in Figure 5, and 6 are shown in Figure 7. The shapes and
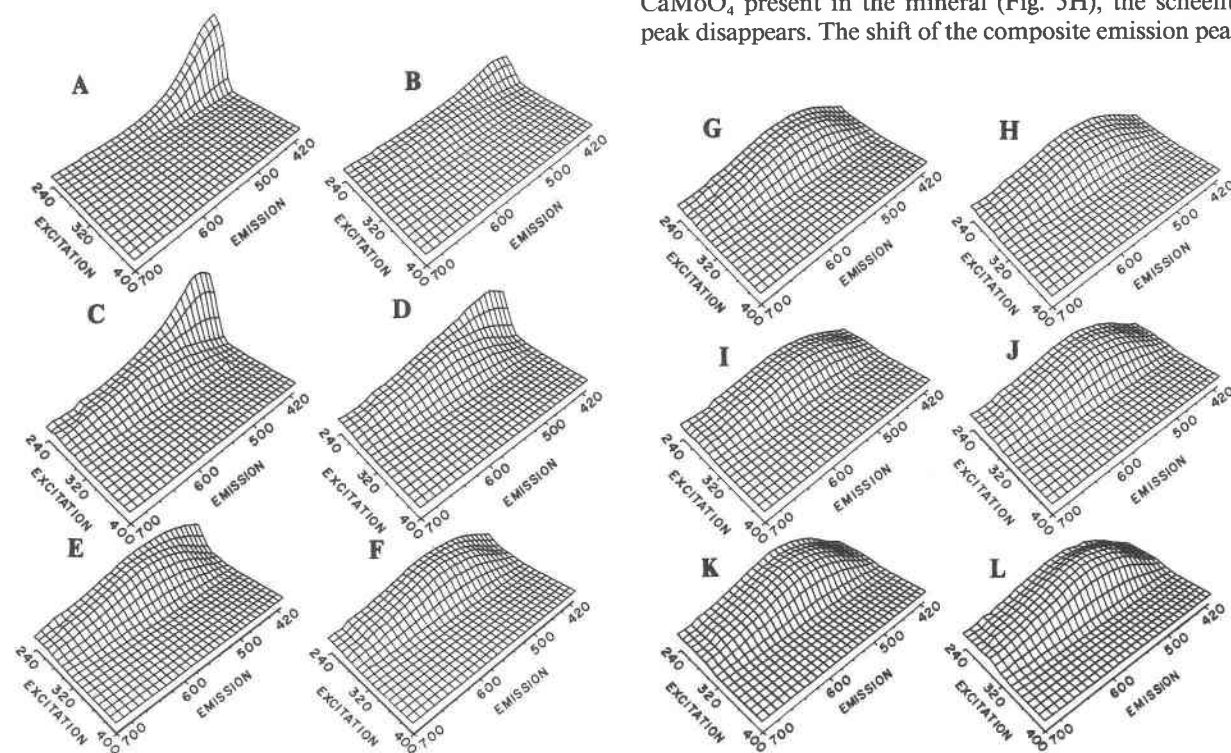
intensities of the other 6 samples (15, 50, 60, 70, 90, and 95 mol% $CaMoO_4$) are similar to the contiguous compositions shown in Figure 5. Instead of one emission peak that changes its position as the composition is changed (Kroger, 1948; Kononov, 1967; Shoji and Sasaki, 1978), two peaks are present in those samples containing less than 10 mol% $CaMoO_4$ (Fig. 5). The emission spectrum at 253.7-nm excitation, noted by Kroger (1948), Kononov (1967), and Shoji and Sasaki (1978), is actually a composite emission peak caused by the combining of the two peaks. Each peak represents the luminescence exhibited by one of the end members. Scheelite exhibits the more intense peak (Fig. 5A). It has maximum excitation and emission at 243 and 425 nm, respectively. The powellite peak (Fig. 5L) appears lower and broader showing maximum excitation at 280 nm and maximum emission at 530 nm. W-rich intermediate members of the series (Fig. 5A–5G) exhibit the pure scheelite and powellite peaks in the same position but at differing intensities.

In this solid-solution series, the first appearance of the powellite peak occurs with 0.2 mol% $CaMoO_4$ present in the scheelite (Fig. 6). The intensity of this peak increases with increasing abundance of $CaMoO_4$, but its position remains constant (Figs. 6 and 7). The scheelite peak exhibits a marked decrease in intensity with as little as 0.2 mol% $CaMoO_4$ present, and as increasingly greater amounts of $CaMoO_4$ are added to the solid solution, the scheelite peak exhibits lower intensities. With 10 mol% $CaMoO_4$ present in the mineral (Fig. 5H), the scheelite peak disappears. The shift of the composite emission peak

Fig. 5. Three-dimensional perspective plots of twelve synthetic scheelite-powellite specimens containing variable amounts of $CaMoO_4$. Parts A and B are at the same gain (1.34). Parts C through L are at a higher gain (3.73). The compositions in mol% $CaMoO_4$ are A, 0; B, 1; C, 1; D, 2; E, 4; F, 6; G, 8; H, 10; I, 20; J, 40; K, 80; and L, 100. The emission and excitation slits were 2.5 and 5.0 nm, respectively.
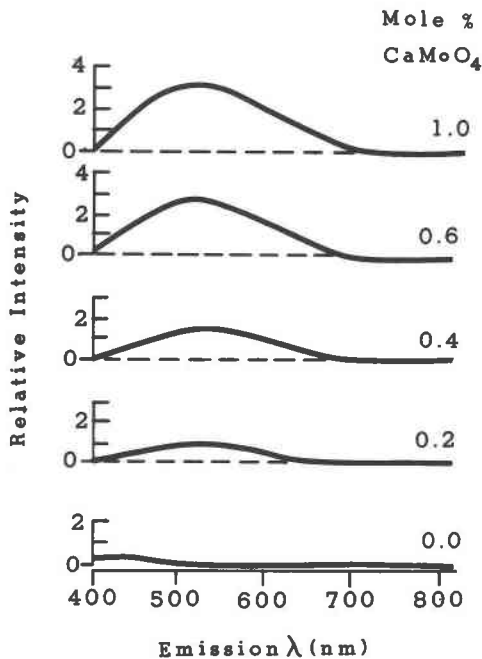
Fig. 6. Emission spectra for five members of the scheelite-powellite solid-solution series. All specimens were excited at 280 nm. Note the appearance of the characteristic powellite peak (530 nm) at 0.2 mol% $CaMoO_4$ and the increase in intensity of this peak at higher concentrations of $CaMoO_4$.

(at 253.7-nm excitation) in the 0–10 mol% $CaMoO_4$ range, as reported by Kroger (1948), Kononov (1967), and Shoji and Sasaki (1978), is a result of the rapid weakening and disappearance of the scheelite peak.

Luminescence mechanisms

The scheelite structure is generally accepted as having $(WO_4)^{2-}$ in the form of slightly distorted tetrahedra that are held apart by Ca^{2+}. Each Ca is surrounded by eight oxygen atoms located at the corners of a distorted cube and shares the corners of its cube with the corners of eight tungstate tetrahedra.

The blue luminescence in scheelite is an intrinsic property of the mineral. The luminescence has been attributed to a charge-transfer electronic transition in the molecular orbital scheme of the anionic tungstate $(WO_4)^{2-}$ complex (see Grasser et al., 1982). The luminescence of powellite (isostructural with scheelite) is also intrinsic and attributed to electronic transitions in molecular orbitals of the molybdate $(MoO_4)^{2-}$ anionic group (Blasse, 1980).

Although the tungstate peak (425 nm; Fig. 5A) has greater intensity than the molybdate peak (530 nm; Fig. 5L), it does not persist as Mo is added to the crystal; it disappears with as little as 10 mol% $CaMoO_4$ present. If the intensity of the tungstate peak were dependent upon the amount of excitation received by the tungstate, the tungstate emission would be proportional to the W:Mo ratio and the strong tungstate peak should be visible to concentrations higher than 10 mol% $CaMoO_4$. Because

this is not the case (Fig. 5), causes other than a dilution of W excitation (and emission) as Mo is added must be occurring. Such causes could include (1) reabsorption of the tungstate emission by molybdate, (2) inhomogeneous distribution of W and Mo in the crystal, (3) locations of the absorption edges of tungstate and molybdate relative to the wavelength of the exciting radiation, (4) thermal quenching of the excitation, or (5) nonradiative migration of energy in the crystal.

In the case of reabsorption, the tungstate luminescence would be reabsorbed by molybdate, either in the same or a different crystal, which then luminesces at 530 nm. This hypothesis fails for two reasons. Molybdate is excited at wavelengths shorter than 350 nm (Fig. 5L), and the tungstate emission (320–570 nm; Fig. 5A) overlaps only the tail of the molybdate excitation. Most of the tungstate light would not be absorbed and some luminescence characteristic of tungstate should be present at $CaMoO_4$ concentrations greater than 10 mol%. Second, if such reabsorption were occurring, its effects should be seen in physical mixtures of pure fine-grained scheelite and powellite. However, a spectrum for a physical mixture containing 70 mol% powellite and only 30 mol% scheelite was recorded and clearly showed the tungstate peak.

Kononov (1967) postulated that the spectral shift resulted from different arrangements of block isomorphism occurring in Mo-bearing scheelites. From 0 to 1.62 mol% $CaMoO_4$, the Mo is present homogeneously throughout the scheelite structure (Kononov, 1967). Above 1.62 mol% $CaMoO_4$, he postulated that Mo in scheelite becomes ordered. At low contents, Mo forms flat grids; with increasing Mo content, two-dimensional layers and eventually multilayer blocks are formed. The layers and blocks become centers of luminescence characteristic of powellite. Inflections in his peak position and peak intensity curves are attributed to the initial formation of these structures (Kononov, 1967). Kononov's (1967) hypotheses on the structure of members in the scheelite-powellite series are not supported by X-ray diffraction analysis. His inflection points were detected neither by us nor other investigators of the scheelite-powellite solid-solution series.

Kroger (1948, p. 135) attributed the shift of the composite emission peak to two characteristics of scheelite and powellite: the locations of their absorption edges and thermal quenching of excitation. An exciting wavelength of 253.7 nm is within the absorption of both the scheelite and powellite components. This excitation, however, is closer to the absorption edge of scheelite (260 nm, sic; we have measured it at 290 nm) than it is to the edge of powellite (340 nm), which allows the powellite component to be more effectively excited. This difference would result in a characteristic molybdate emission stronger than that indicated by the W:Mo ratio (Kroger, 1948, p. 135).

At temperatures below −180 °C, the strength of the characteristic tungstate and molybdate emissions would reflect the efficiency of their relative excitations (Kroger, 1948, p. 135). At room temperature, however, Kroger (1948, p. 135) surmised—incorrectly, we believe—that
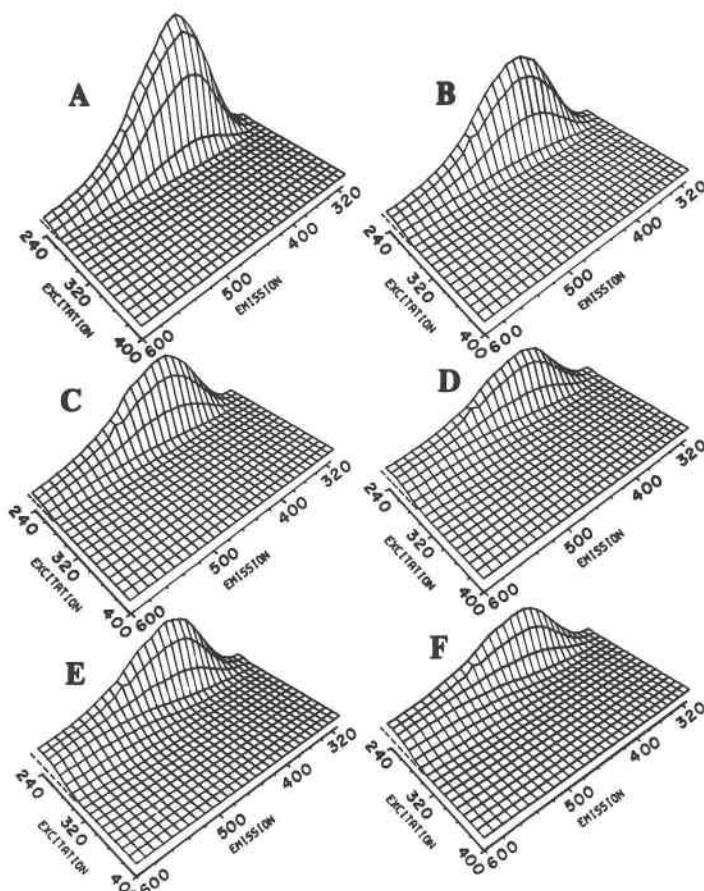
Fig. 7. Three-dimensional perspective plots of six synthetic scheelite-powellite specimens having 0 to 1 mol% CaMoO₄. The compositions in mol% CaMoO₄ are A, 0.0; B, 0.2; C, 0.4; D, 0.6; E, 0.8; and F, 1.0. The emission and excitation slits were 2.5 and 5.0 nm, respectively.

thermal quenching of tungstate excitation would be more efficient than thermal quenching of molybdate excitation, and the intensity of the characteristic tungstate luminescence relative to molybdate emission would be reduced. Kroger envisioned that both processes caused the shift in composite emission. Recent investigations, however, have shown that excitation at 253.7 nm is away from the absorption edges of both scheelite and powellite (this study) and that, at room temperature, thermal quenching is more efficient for powellite than for scheelite (Powell and Blasse, 1980).

A possible explanation for the marked decrease in the intensity of the tungstate peak when as little as 0.2 mol% CaMoO₄ is added may be a nonradiative migration of energy within the crystal. The process of energy migration from sensitizer (absorbs energy) to activator (emits energy) elements in artificial phosphors has been studied in detail (e.g., Powell and Blasse, 1980). The work has centered around the addition of trace amounts of rare-earth elements (REEs) or transition metals to inorganic compounds such as halides, vanadates, borates, and phosphates (Imbusch, 1978; Powell and Blasse, 1980). For instance, fluorapatite, when doped with Sb and Mn, will

luminesce. In this case, Mn is the activator, but it can only be excited by the migration of energy from a sensitizer, specifically Sb (Imbusch, 1978). The effect of the dopants is strongly dependent on their concentration in the host crystal because the energy-migration process is dependent on the distance the energy must migrate between a pair of atoms in each transfer. There can be a number of such transfers between sensitizers before the energy reaches an activator. Too high a concentration of the REEs in the host, however, may lead to quenching of the excitation without producing luminescence (Powell and Blasse, 1980).

The scheelite end member does allow energy migration at room temperature (Powell and Blasse, 1980, p. 66). The spectra seen in this study can be explained by a migration of the excitation energy from a tungstate to a molybdate where it is trapped and luminescence characteristic of molybdate can occur (Fig. 8). The energy differences between the ground and excited states in tungstate are greater than those in molybdate. The higher energy gaps in the tungstate relative to the molybdate are evidenced by the peak excitation for tungstate (243 nm; 5.10 eV) versus molybdate (280 nm; 4.43 eV) and the
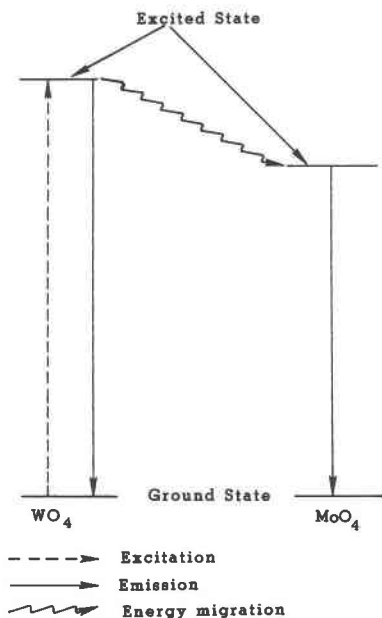
Fig. 8. A schematic illustration of the process of nonradiative energy migration. The tungstate is excited and transfers the energy to molybdate, which luminesces.

peak emission for tungstate (425 nm; 2.92 eV) versus molybdate (530 nm; 2.34 eV). The energy gaps allow for a one-way migration of the energy into the molybdate orbitals because it cannot return to the higher energy gaps of the tungstate (R. C. Powell, oral comm., 1985). Any energy that migrates to the molybdate is effectively trapped (Fig. 8). For zero tungstate emission to occur, Mo atoms must be close enough to W atoms in the crystal lattice to allow the energy to migrate to the molybdate before a tungstate emission occurs. Apparently, with as little as 10 mol% $CaMoO_4$ and a homogeneous distribution of Mo in the crystal structure, energy migration to molybdate and zero tungstate emission do occur.

FLD DETECTION

Prediction of detectivity by the FLD

The FLD uses the Fraunhofer line-depth method of measuring luminescence, which involves observing a selected Fraunhofer line in the solar spectrum and measuring the ratio of the central intensity of the line to a convenient point on the continuum a few tenths of a nanometer distant. This ratio is compared with a similar ratio of a conjugate spectrum reflected from material that is suspected to luminesce. Both ratios normally are identical, but luminescence is indicated where the Fraunhofer line profile in the reflected spectrum is filled in, and the reflected target ratio exceeds the solar reference ratio. Therefore, the Sun can be used as an excitation source without complete masking of any luminescence which is produced (Hemphill et al., 1983a, 1983b).

In order to assess whether luminescing materials would be detectable with a FLD before conducting an airborne survey, the spectral luminescence intensity of a sample target material may be measured with the fluorescence spectrophotometer (Fig. 1). The spectrophotometer can be operated so as to produce excitation spectra; the excitation monochromer is scanned while the emission monochromer is stationary at the wavelength of a specific Fraunhofer line. This arrangement provides a system in the laboratory analogous to a FLD in the field, where broadband excitation of the Sun (>300 nm; Luckiesh, 1946, p. 48) produces an emission in a luminescent material, the intensity of which is monitored at one or more Fraunhofer lines. The spectra are corrected initially for wavelength variation in spectrophotometer source and detector by means of the CSU. To acquire the same wavelength and intensity dependence of luminescence in the laboratory as would be observed with an airborne FLD, the source- and detector-corrected spectra are also convolved with the spectral intensity of direct sunlight and diffuse skylight, using radiation data from Kondratev (1973, p. 417; acquired before noon, September 24, 1962, Odessa, USSR, lat 46°N) and/or Luckiesh (1946, p. 48; acquired midsummer, Cleveland, U.S.A., lat 41.5°N).

By comparing these results with excitation spectra of a rhodamine WT dye standard upon which the same corrections have been applied, the luminescence intensity of a sample material at one or more Fraunhofer lines may be expressed as a certain concentration of rhodamine dye that has equivalent intensity (Hemphill et al., 1977; Watson, 1981). The level of luminescence intensity adjudged to be significant is 2.0 ppb rhodamine dye equivalency or larger and is based upon demonstrated sensitivity of the FLD when operated from aircraft. Although under ideal test conditions, the FLD is sensitive to rhodamine dye at concentrations as small as 0.1 ppb (Plascyk and Gabriel, 1975), airborne remote sensing of luminescence can be adversely affected where size of outcrop is smaller than the sensor pixel, where atmospheric dust and aerosols obscure the outcrop, and where nonluminescent materials such as detritus and vegetation reduce luminescence intensity.

Rhodamine dye equivalencies

Rhodamine dye equivalencies of 17 synthetic specimens are reported for the Fraunhofer lines at 486, 518, 589, and 656 nm (Table 3). Their values range from 0 to 7.5 ppb. The values typically increase as the samples become more Mo rich.

Of the four lines, 518 nm appears to be the most sensitive to the compositional changes in the samples. Equivalencies for this line vary from 0.6 to 7.5 ppb. The composition where the scheelite should be detectable by the FLD (2 ppb) is 8 mol% $CaMoO_4$, although 6 mol% $CaMoO_4$ yields an equivalency of 1.9 ppb. All samples having >8 mol% $CaMoO_4$ have rhodamine dye equivalencies greater than 2 ppb. The highest equivalency is exhibited by pure powellite.

The Fraunhofer lines at 486 and 589 nm show equivalencies of 2 ppb and higher at a composition ≥15 mol%

CaMoO$_4$. The line at 656 nm exhibits equivalencies of 2 ppb or greater for all compositions having ≥50 mol% CaMoO$_4$. These three lines also exhibit their highest equivalencies at pure powellite.

The addition of 8 mol% CaMoO$_4$ to scheelite will increase its solar-stimulated luminescence to a level detectable by the FLD operating at 518 nm. Although scheelite and powellite exhibit complete solid solution, few intermediate members occur naturally. Most natural scheelites contain less than 5 mol% CaMoO$_4$ (Hsu and Galli, 1973).

The low number of scheelites containing more than 8 mol% CaMoO$_4$ would suggest that FLD detection of this mineral species would be limited. To test this conclusion, we measured luminescence in 85 natural scheelite samples using the spectrophotometer. We have found significant luminescence in all natural scheelites that contain >8 mol% CaMoO$_4$ (7 samples). Forty-three of the scheelite samples containing <8 mol% CaMoO$_4$ (12 with no detectable Mo) exhibited luminescence at intensities greater than 2 ppb rhodamine dye equivalency. Although Mo content in scheelite is a major contributing factor to luminescence, it appears that other factors must be considered when determining whether natural scheelite is detectable by the FLD. The data and causes (probably impurities or structural defects) of the luminescence and the feasibility of FLD detection are discussed in detail in Hemphill et al. (1988).

CONCLUSIONS

The emission peak (at 253.7-nm excitation) in Mo-bearing scheelite is actually a composite peak formed by the addition of characteristic tungstate (425 nm) and molybdate (530 nm) emissions. The characteristic emissions do not change their positions as composition is varied; rather their intensities change. The intensity of luminescence characteristic of tungstate decreases to zero with the addition of only 10 mol% CaMoO$_4$ and probably represents nonradiative energy migration from the tungstate to the molybdate. The marked decrease in the tungstate peak as Mo is added causes the sharp shift in the spectra of the composite emission peak.

Although spectra of the synthetic samples indicate that only those scheelites having ≥8 mol% CaMoO$_4$ should luminesce, under solar stimulation at intensities high enough for detection by the FLD, many natural scheelites containing <8 mol% CaMoO$_4$ show significant luminescence. These natural scheelites may contain impurities or structural defects that may enhance their solar-stimulated luminescence.

TABLE 3. Rhodamine WT dye equivalencies for 17 synthetic scheelite-powellite specimens

Mol% CaMoO$_4$	Fraunhofer lines			
	486 nm	518 nm	589 nm	656 nm
0	0.5	0.6	0.3	0
1	0.6	0.9	0.5	0.1
2	1.1	1.3	0.8	0.2
4	1.5	1.7	1.1	0.3
6	1.7	1.9	1.4	0.5
8	1.9	2.0	1.6	0.5
10	—	2.4	2.0	0.7
15	2.7	2.9	2.5	0.9
20	2.9	3.2	2.7	0.9
30	2.8	3.3	2.9	1.2
40	3.4	3.9	3.3	1.8
50	4.3	5.2	4.4	2.7
60	4.2	5.0	4.5	2.6
80	6.2	5.8	5.4	2.9
90	6.8	6.6	6.1	3.8
95	6.3	6.9	6.3	4.1
100	7.2	7.5	7.0	4.8

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