

Variations in unit cell parameters and in the X-ray diffraction intensity ratio $I(200)/I(100)$ in the lazulite–scorzalite series

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Abstract

Lattice parameters and X-ray powder diffraction intensity ratios were measured for members of the lazulite–scorzalite series, ranging from 23 to 95 mole percent lazulite. The b , c , and V values increase linearly with percent scorzalite, b showing a lower correlation with composition than c or V . The correlation is not strong enough to use these parameters to estimate accurately the position in the series. The a dimension appears to be independent of composition. The intensity ratio $I(200)/I(100)$, measured by X-ray powder diffractometry, correlates strongly with composition, permitting chemical characterization using the equation, mole-percent lazulite = $15.5y - 0.51y^2 - 0.92$, where y is $I(200)/I(100)$. Accuracy with this method is estimated to be 3–4% lazulite.

Introduction

Chemical analyses of lazulite and scorzalite reported by Pecora and Fahey (1949a,b; 1950) and others (Campbell, 1962; Fransolet, 1975; Igelström, 1855; Meyers, 1948; Palache and Gonyer, 1930) suggest that there is complete solid solution from lazulite, $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$, to scorzalite, $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$, although material high in iron is rare. Research by Lindberg and Pecora (1955) indicates that barbosalite, the ferric iron analog of scorzalite, is isostructural with scorzalite, but has a larger unit cell. According to Lindberg and Christ (1959) the existence of a complete solid solution has not been established between scorzalite and barbosalite; however, ferric iron may substitute for aluminum in scorzalite in amounts up to 2.98 weight percent (Henriques, 1957; Pecora and Fahey, 1950; Kuznetsova, 1972; and Lugovskoi, 1965).

Determination of specific composition in the lazulite–scorzalite series is fraught with difficulties. Members of this series are insoluble in common acids, which complicate analyses by wet chemical methods and by instrumental methods which require prior solution. Furthermore, methods requiring solution may be in error due to the presence of alteration and inclusions. Due to the difficulty in obtaining standards of suitable matrix, analysis by electron probe instruments is not a very satisfactory alternative. Members of the series commonly have many inclusions, making specific gravity an unreliable indicator of composition.

In order to identify a useful parameter for reliably estimating composition from X-ray diffraction data, we have investigated variations in lattice parameters and in X-ray diffraction intensities through the lazulite–scorzalite series.

Methods

Seventeen samples of lazulite–scorzalite were analyzed chemically for Fe, Mg, and Al and were analyzed by X-ray powder diffractometry for selected relative intensity ratios. Eleven of these samples were available in sufficient quantity to mix with silicon for determination of lattice dimensions by X-ray powder diffractometry.

A lithium tetraborate fusion was employed to dissolve a hand picked sample of each mineral, and the resulting glass was dissolved with agitation in HCl. Mg, Al, and Fe in the acid solution were determined using atomic absorption spectrophotometry. Atomic absorption reference solutions were used to make standards, and, to avoid matrix effects, a blank of lithium glass was added to the standards in the same proportion as contained in the mineral solutions.

A General Electric XRD-5 diffractometer and $\text{CuK}\alpha$ radiation were used for all X-ray analyses. Each sample was sieved to less than 325 mesh and 7/1 mixture of collodion and amyl acetate was used to prepare smear mounts on glass slides.

For measurement of unit cell parameters scans were made at $0.2^\circ 2\theta$ per min from 12° to $90^\circ 2\theta$

using a 3° divergence slit, MR Soller slit, 0.1° detector slit, 2° take-off angle and a graphite (002) monochromator. Silicon (NBS SRM-640) was used as an internal standard to correct all observed 2θ angles. The weighted average wavelength (1.54178) of CuKα radiation was used to convert low and moderate 2θ angles to *d* values. Where the diffraction lines were resolved clearly into α₁ and α₂ components the α₁ wavelength (1.54056) was used. For each sample, *d* values from the same 16 reflections were used in a computer program designed to calculate a least-squares refinement of lattice dimensions (Appleman and Evans, 1967). Reflections were chosen which had only one contributing family of planes and were completely resolved from other reflections. Corrected *d* values were used in conjunction with a 1/*d*² weight factor to minimize the larger errors inherent at lower angles.

Calculated diffraction patterns, using the computer program of Clark, Smith, and Johnson (1973), the crystal structure parameters of Lindberg and Christ (1959), and observed patterns, indicated that the intensity ratio, *I*(200)/*I*(100), might be a reliable and sensitive indicator of position in the series. The intensities of the (200) and (100) reflections were chosen as a measure of Fe,Mg substitution because both intensities vary considerably with ferrous iron content. Other strong reflections [(011); (112); and unresolved (111), (211)] which change in intensity through the series were examined and were not found to be reliable indicators of composition. In addition, the (200) and (100) intensities should be equally influenced by any preferred orientation, and, therefore, the ratio *I*(200)/*I*(100) should not be influenced strongly by the method of sample preparation. The peak height intensities of the (200) and

Table 1. Lattice parameters of lazulite-scorzalite

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
5	7.155(2)	7.301(2)	7.250(1)	326.1(1)
6	7.156(2)	7.277(3)	7.239(2)	324.8(1)
2	7.146(2)	7.284(2)	7.237(2)	324.6(1)
12	7.145(2)	7.279(2)	7.233(2)	324.1(1)
8	7.149(1)	7.283(2)	7.240(1)	324.9(1)
4	7.149(2)	7.284(2)	7.236(1)	324.6(1)
9	7.148(2)	7.286(2)	7.234(1)	324.6(1)
1	7.152(3)	7.273(3)	7.236(2)	324.2(1)
10	7.146(2)	7.274(3)	7.230(1)	323.8(1)
3	7.148(2)	7.283(2)	7.233(1)	324.4(1)
11	7.150(1)	7.273(2)	7.234(1)	324.0(1)

Parenthesized figures represent the estimated standard deviation.

Table 2. Chemical analyses for 17 samples of lazulite-scorzalite

Sample	Location	Mg/Fe	FeO	MgO	Al ₂ O ₃
17 *106631	Victory mica mine Custer, SD	23	16.5	2.77	29.6
14 *106693	Champion mine Mono County, CA	30	16.2	3.82	30.1
5	Pennington County, SD	27	14.7	2.97	30.8
16 *5862	Minas Gerais, Brazil	33	13.8	3.74	29.5
2	Champion mine Mono County, CA	67	7.07	7.89	30.5
6	Jackson County, OR	63	7.07	6.70	28.6
7 *126894	Horrnsjoberget Sweden	72	6.56	9.27	29.8
15 *94265	Mono County, CA	71	6.47	8.71	30.0
12	Palermo mine, NH	71	6.22	8.70	29.1
8	Belafa, Madagascar	74	5.80	9.39	30.4
4	Horrnsjoberget, Sweden	75	5.37	9.07	31.5
9	Gaston County, NC	78	4.95	9.58	30.9
13 *15674	Diamantina, Brazil	82	4.11	10.6	30.9
1	Arizona	80	4.11	9.24	31.5
10	Graves Mt., GA	83	3.26	9.24	30.9
3	Blow River, Canada	87	2.84	10.8	31.5
11	Werfen, Austria	95	1.14	12.2	30.6

* Indicate sample (and number) from the National Museum of Natural History

(100) reflections were measured for each of the 17 samples by making 10 scans at 0.4° 2θ per min through an angular range of 13° to 16° and 25° to 31° 2θ. Scans were made using a 1° divergence slit, MR Soller slit, 0.1° detector slit, 6° take-off angle and a Ni filter on smear mounts consisting of 110 mg of the mineral. Slides prepared by sprinkling the mineral onto a vaseline-covered slide gave similar intensities; however, this method was discarded due to the lack of precision. Intensity measurements from the sprinkled mounts varied much more than those from the smear mounts and usually were not reproducible once the slide had been moved.

Results and discussion

Lattice parameters

The unit cell dimensions and volumes of 11 chemically analyzed members of the lazulite-scorzalite series are listed in Table 1, and scatter

diagrams constructed from these data and from the chemical analyses (Table 2) are shown in Figure 1. In order to evaluate the relationship between lattice parameters and the Fe/Mg ratio, the least-squares regression line and the coefficient of determination (r^2) were calculated for each set of data.

Figure 1 shows that variation of the a dimension is virtually independent of composition. The data points are not arranged in a linear or curvilinear pattern, although, due to the prevalence of samples of ferroan lazulite, there is a cluster of points in the high magnesium region. The coefficient of determination for these data is 0.26, indicating that only 26% of the variability in a may be accounted for by changes in composition. The limiting values of a , 7.145 and 7.156 Å, correspond to compositions of L71 and L63, respectively, and thus only a narrow range in composition is represented by the two extreme values of a . The values of b plotted against composition show a linear trend, increasing with ferrous iron content. The r^2 for the data is 0.65. The values of b vary from 7.273 Å for a composition of L95 and L80 to 7.301 Å for a composition of L27. These samples are near the end-member compositions; thus the total change in b through the series is approximately 0.028 Å. The c lattice dimension shows a strong correlation with composition. In these data, 78% of the variation in c is associated

with a concurrent change in composition ($r^2 = 0.78$). The values increase from 7.230 Å to 7.250 Å as the percentage of scorzalite increases. Examination of the data reveals that any attempt to use c to estimate composition could result in a large error. For example, 7.233 Å corresponds to one chemically-determined composition of L71, whereas the composition estimated from the regression line would be L86, a 15% error. In Figure 1, the unit cell volume correlates well with composition as it consistently increases with iron content. The volumes range from 323.8 to 326.1 Å³. This range is considerably greater than that of a , b , or c (0.011, 0.028, 0.020, respectively), however, the r^2 for the unit cell volume-composition regression line is 0.78. Therefore, it is no more accurate to predict composition from unit cell volume than from the c dimension alone.

The results described above are not surprising. The unit cell dimensions change only slightly through the series, due to the similarity of the ionic radii of Mg²⁺ and Fe²⁺. Although b , c , and V are dependent on the Fe/Mg ratio, the total variation of lattice parameters is so slight that, except for major compositional changes, the variation exceeds the accuracy of the measurements. For instance, c changes by approximately 0.016 Å between end members of the series. The errors listed in Table 1

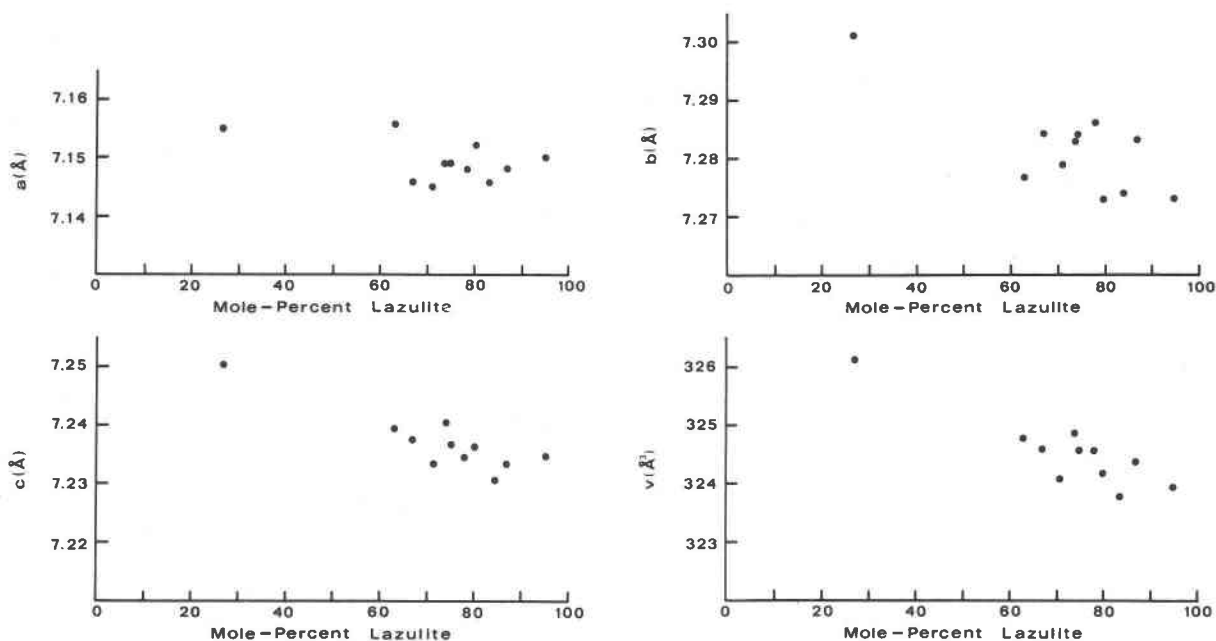


Fig. 1. Scatter diagrams showing the lattice parameters a , b , c , and V for 11 samples of lazulite-scorzalite plotted against composition.

show that the error of the refined values of c ranges from 0.001 to 0.002Å, which is roughly 10% of the total variation of c .

The intensity ratio $I(200)/I(100)$

Because the atomic number of Fe (26) is more than twice that of Mg (12), the atomic scattering factors of these elements are considerably different, and this difference causes a substantial variation in the intensity of some reflections as Fe substitutes for Mg. For instance, the intensity of the (200) reflection increases and the intensity of the (100) reflection decreases as the percentage of lazulite increases.

Multiple measurements of the intensities of the (200) and (100) reflections were made and, to eliminate undue influence from extreme measurements, the median values were used to compute $I(200)/I(100)$. Figure 2 shows that the intensity ratios of the 17 samples of the lazulite-scorzalite series increase with mole percent lazulite. Although the observed intensities appear to vary almost linearly with composition, a quadratic equation yields an r^2 of 0.99 compared with an r^2 of 0.96 for a linear model. The data show the following relationship between peak height ratio and the amount of lazulite component in the mineral: mole percent lazulite = $15.5y - 0.15y^2 - 0.92$.

Summary

Unit cell parameters b , c , and V are linearly related to composition, with b showing a slightly lower correlation than c or V . Nonetheless, based on the data reported in this study, and assuming comparable accuracy, neither c nor V can be used to accurately predict composition. A close approximation of composition is not possible because the total change of these parameters through the series is very small, due to the similar size of Fe^{2+} and Mg^{2+} ions. As a result, slight variations in composition cannot be detected by this method. The a dimension appears to be virtually independent of composition. The intensity ratio $I(200)/I(100)$, determined by powder diffractometry, increases predictably and rapidly as the composition of lazulite-scorzalite changes through the series from $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$ to $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$. Once the ratio $I(200)/I(100)$ has been measured, the composition of a given sample of lazulite-scorzalite may be calculated from the equation, mole-percent lazulite = $15.5y - 0.51y^2 - 0.92$. Accuracy with this method is estimated to be within 3–4 percent lazulite.

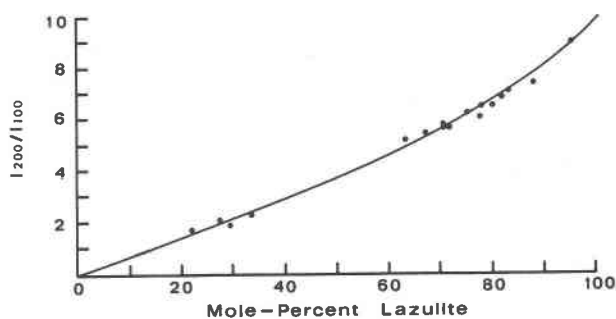


Fig. 2. Scatter diagram showing the X-ray diffraction intensity ratio $I(200)/I(100)$ for 17 samples of lazulite-scorzalite plotted against composition.

lite. The coefficient of determination for this equation is 0.99.

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