MINOR ELEMENTS IN QUARTZ

THESIS FOR DEGREE OF MASTER OF SCIENCE
MICHIGAN STATE UNIVERSITY

JOHN J. KUDLAC

THESIS

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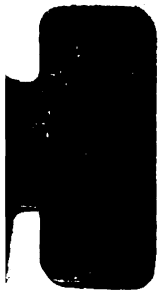

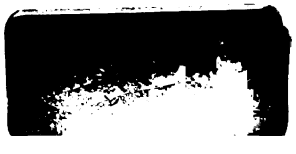

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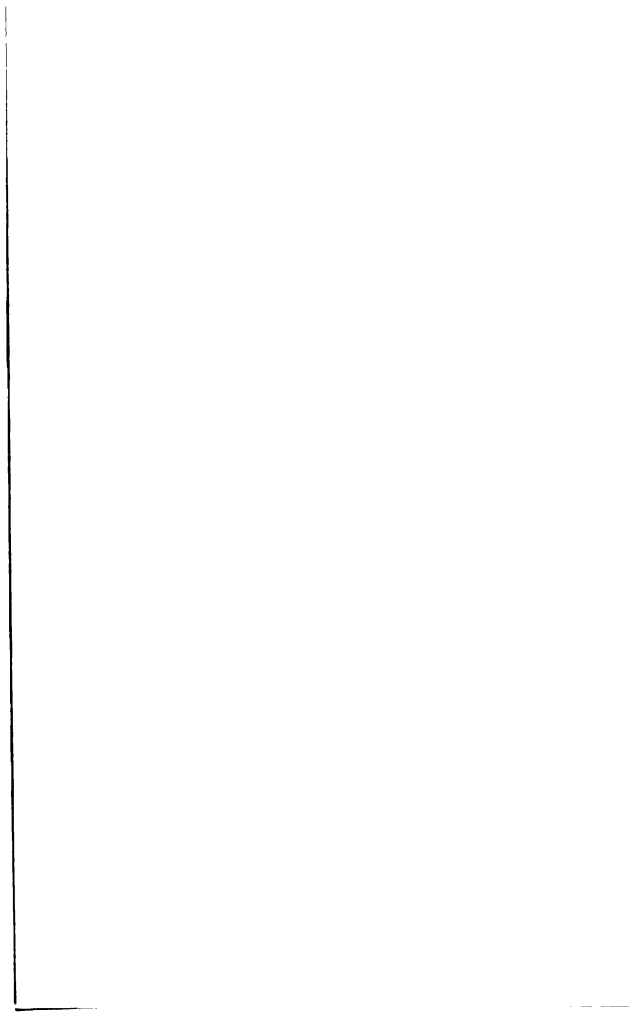

MINOR ELEMENTS IN QUARTZ

by

John J. Kudlac

A Thesis

Submitted to the College of Natural Science

Michigan State University

in partial fulfillment of the requirements

for the degree of

Master of Science

Department of Geology

1965

MINOR ELEMENTS IN QUARTZ

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Michigan State University, 1965

Abstract - Twenty-four clear, crystalline quartz samples were analyzed for their impurity content. It was found that Aluminum is the major impurity, with Fe, Ti, Mg, Cr, Ca, Cu and Ag present in smaller amounts.

The unit cell dimensions of the samples were also obtained and were found to vary by a significant amount (a_o varied from 4.9058Å to 4.9093Å and c_o from 5.3932Å to 5.4025Å).

A plot of the aluminum content versus unit cell dimensions showed that the dimensions vary with aluminum content; however, no particular relationship exists.

In plotting the axial ratio versus "increment ratio", it was found that as the axial ratio increased the "increment ratio" increased. This suggests that as a_o increases, c_o increases. The increase in cell dimensions is due to the increase in both substitutional and interstitial impurities. An examination of specific samples showed that an increase in a_o and c_o with increasing impurity content is caused by a proportional increase in both substitutional and interstitial impurities.

ACKNOWLEDGMENTS

The writer is grateful to Dr. H. R. Stonehouse for suggesting this problem and for guiding the work through its various phases.

Appreciation is also extended to Dr. J. Zinn and Dr. W. J. Hinze who critically read this thesis.

The writer would especially like to thank his wife, Patricia whose patience and fortitude made possible the completion of this thesis.

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I. INTRODUCTION

In this study, twenty-four quartz crystals were analysed for their minor element content in order to test the validity of Miller's (1960) conclusion that the electronic configuration of an ion is the major factor in determining the ability of an impurity to substitute isopositionally in a given structure. The unit cell dimensions of the quartz crystals have been obtained in order to determine the variation, if any, of cell size with impurity content.

A. Background

In recent years the behavior of trace elements during the fractional crystallization of a melt has been the subject of intense investigation. Goldschmidt (1937) initiated these studies, when he proposed the following rules governing the distribution of trace elements among magmatic minerals. He assumed largely that ionic bonding prevails and that the ion making the larger contribution to the energy of the crystal structure is prefered.

> (1) For two ions to substitute diadochally one for another in a crystal structure, the ionic radii must not differ by more than 15%.
>
> (2) When two ions possessing the same charge, but different radii, compete for a position in a crystal structure, the ion with the smaller radius is prefered.
>
> (3) Ions having similar radii but different charges (of the same sign) may substitute diadochally in a crystal; in which case the ion having the larger charge has preference over the ion with the smaller charge.

However, the assumption that ionic bonding prevails in a crystal structure has been proven to be erroneous. Studies on bond lengths, bond energies etc. have indicated that, in general, a bond between two unlike atoms cannot be described as being

purely ionic or convalent, but will be some combination of the extreme types, or will be a hybrid bond, resonating between the two extreme forms. One of the classical differences between ionic and covalent bonding is that where ionic bonding predominates there are no special restrictions on the bonds and the radius ratio rule will apply; that is, the particle (ion) position will depend on relative sizes of the cations and anions. However, the particle positions, where covalent bonding predominates, are largely determined by the directional properties of the bond. For example, the silicon atom forms four bonds directed toward the corners of a regular tetrahedron. Therefore, it is of importance in analyzing a structure to know approximately what type of bond exists in particular minerals.

The extent to which atoms form ionic or covalent bonds depends largely on two factors: ionization potential and electron affinity. These two factors are combined into what is known as the electronegativity of an atom. Pauling (1960) related the difference in the electronegativity of atoms to the type of bond that will form between them. Fyfe (1951), using electronegativity as an indication of bond type, showed that in ionic compounds two atoms will be mutually replaceable if their sizes are similar, and that in more covalent compounds, the atoms will be replaceable only if the number and directional properties of their bonds are similar.

Ramberg (1952) showed that the distribution of metals among silicates is only partly governed by the size and the charge of the

ions. He states that the substitution of the metals for one another in silicates is also dependent on the variable electronegativity of the oxygen in the structure and the position of the metals in the electronegativity scale. The value of the electronegativity of the oxygen in the different silicate structures increases stepwise from the orthosilicates to the tectosilicates.

Shaw (1953) shows, by a theoretical treatment of and an experimental approach to binary systems, that it is impossible to predict whether a trace element will be concentrated in early or late mineral fractions on the basis of ionic radii. DeVore (1953) suggests that the differences of the polarizing power of the different cations as related to the polarizabilities of the anions explains the distribution and fractionation of elements during crystal growth. The ionization potential of the cations provides the best measurement of the polarizing power of the cation.

Ahrens (1952, 1953) again stresses the significance of ionization potentials as a factor in predicting the behavior of elements during the crystallization of a magma. Ringwood (1955a,b) discusses the influence of electronegativity and the role of complex formation as factors governing the distribution of trace elements.

Because silicates make up a great portion of the rock forming minerals, it is important to mineralogists, petrologists and geochemists to have a better understanding of the crystal structure of the silicates and the elements occupying specific positions in their framework. W. L. Bragg (1930) outlined the general nature of many crystalline

silicates by means of X-ray diffraction studies. The isopositional replacement of Ga(III) and Ge(IV) for Al(III) and Si(IV) in sodium and potassium feldspars was investigated by Goldsmith (1950).

Colemane (1962) synthesized diopsides and investigated the effect of ionic substitution on their unit cell dimensions. Miller (1960) studied the effects of Ga, Fe, Cr, Co, and V substituting into the crystal lattice of $ALPO_4$, which has a close structural similarity to $SiSiO_4$ (α-quartz). He concludes, from this investigation, that the electronic configuration of the ion, and not the ionic radius, is the principle factor in determining the ability of an impurity to substitute isopositionally in a given structure.

II. CRYSTAL CHEMISTRY OF ALPHA-QUARTZ

The structural crystallography of quartz was among the first to be investigated by X-ray methods (Bragg 1914) and received attention from many other workers before it was determined by Gibbs (1926). More detailed studies were subsequently carried out by Wei (1935) and Machatschki (1936). Quartz has a crystal structure based on an hexagonal lattice. The unit cell, containing three SiO_2 molecules, has the nominal dimensions, $a_o = 4.913\text{Å}$ and $c_o = 5.405\text{Å}$ (Swanson et al. 1954).

In the structure of quartz, the silicon atoms are in four-fold coordination with oxygen and make up the SiO_4 tetrahedra. This unit is basic to the structure of all the known polymorphs of silica and the silicates in general. The exception is stishovite where the silicon atom is octahedrally coordinated. The tetrahedral configuration of the Si-O bonds is the result of hybridization of the 3s and $3p^3$ orbitals of silicon.

Each oxygen, in the quartz structure, is shared with two silicon atoms. Thus, the SiO_4 tetrahedra are linked by the sharing of each of the corner oxygen atoms. The resulting arrangement is a three dimensional framework. The SiO_4 tetrahedra, in quartz, are almost symmetrical, with a Si-O bond distance of 1.61Å. The Si-O bond is of the intermediate type, roughly 50% ionic and 50% covalent.

Many workers have found that the cell dimensions of quartz vary significantly. However, neither the range of variation nor the dimensions for the pure end-composition have been clearly established. These variations in lattice parameters have been attributed to the presence of foreign ions, the presence of lattice defects (vacancies) and the influence of temperature

and pressure at the time of crystallization. Sabatier and Wyart (1954) found that the physical conditions of crystallization hardly affected the lattice parameters of synthetic quartz. However, they were affected by traces of sodium impurities. Keith (1955), on the other hand, had found that the cell parameters of synthetic crystals, which had been grown at higher temperatures, were smaller. Keith and Tuttle (1952) found that the differences of cell parameters were accompanied by small differences of the α-β inversion temperature. Both variations are probably associated with solid solution of impurity ions. Kamentsev (1963) employs theoretical arguments to show that the temperature of crystallization governs the amount of solid solution in the quartz structure, and hence that the temperature of formation controls the variation of the unit cell parameters. He concludes that the amount of structural impurities and the unit cell parameters decrease the higher the temperature of crystallization and thus, it seems that the unit cell dimensions of quartz would be affected by the variation in the minor element content.

Quartz, in its chemical composition, is almost 100% SiO_2. There is, however, a small range of variation which may be due to a limited amount of substitution, to small inclusions of other minerals, or to the liquid infillings in cavities within the quartz. Lithium, sodium, aluminum and titantium are the principle elements that enter into solid solution with natural quartz. Magnesium, iron, calcium and potassium may also be present in significant amounts and a number of other elements have been reported in smaller quantities. Germanium, due to the similarity of its ionic radius to silicon's and due to its

position in the periodic table, is one probable element for substitution in natural quartz, but it is generally not found.

Aluminum is the major element to substitute for silicon in quartz. To compensate for the valence defficiency, small alkali ions, Li or Na, or both, enter the structure into interstitial positions. Other possible combinations are: three substitutional aluminums plus one interstitial aluminum and two substitutional aluminums plus one interstitial magnesium. The maximum extent of the substitution by aluminum in quartz is not clearly established. The content of aluminum in quartz ranges from 10-500 ppm.

In general, the unit cell volume increases with increasing amounts of aluminum. According to Cohen and Sumner (1958), the substitution of aluminum for silicon increases both a_o and c_o, although not equally, while the interstitial type of solid solution mainly expands a_o. Keith and Tuttle (1952) showed that the amount of aluminum present in solid solution increases with increasing temperature of formation of quartz as indicated by the variation in the high-low inversion temperature of samples taken from different environments. This same increase of aluminum content with increasing temperature was also indicated by the variation in the unit cell dimensions of certain samples of synthetic quartz (Frondel and Hurlbut, 1955; Keith and Tuttle, 1952). These observations seem to contradict the conclusions drawn by Kamentsev (1963) mentioned previously. However, neither the numerical relation between the amount of aluminum in solid solution and the unit cell dimensions nor the maximum variation in the amount of aluminum or in the unit cell dimensions have been determined.

Keith (1955) studied the unit cell dimensions of four quartz samples and their "increment ratios" ($\Delta a/a/\Delta c/c$). In this study, Δa and Δc are the differences of a and c between any two samples of quartz. By comparing these ratios to the ratio of the strain components of quartz, he concluded that impurities should cause a stress in the quartz lattice and thus the parameters and that the effect should be greatest in the plane normal to the optic axis.

Cohen (1958) using Keith's "increment ratio" made a comparison of the cell dimensions reported in his work. Keith's Brazilian quartz was chosen for comparison purposes as being of low impurity content. Its cell dimensions are $a_o = 4.9129$Å and $c_o = 5.4045$Å (25°C). By comparing the "increment ratio", axial ratio, lattice constants, impurity analysis and color center formation, he concludes that, as a generallization, cationic impurities in quartz may be substitutional replacing Si^{+4}, or interstitial. He also proposes rules (generallizations) which may be used to gain information concerning impurities present where "increment ratios" and axial ratios correlate. The assumptions made are that interstitial impurities mainly cause expansion of the a axis and substitutional impurities cause expansion of both axes. The following are the rules:

> (1) a low "increment ratio" (~1.5 or less) indicates the -quartz contains mainly substitutional impurities and these impurities have radii larger than Si^{4}.
>
> (2) an intermediate "increment ratio" (~1.4 - 1.7) indicates both substitutional and interstitial impurities are present.
>
> (3) a high "increment ratio" (>1.7) or lack of correlation between this and the axial ratio indicates a high percentage of the impurity is interstitial.

In a later paper, Cohen (1960) studied samples of synthetic quartz, by x-irradiating them and by heating them beyond the β-transition temperature and letting them cool to room temperature. From the results of these experiments he concludes that aluminum may be incorporated into α-quartz either interstitially or substitutionally and that the interstitial aluminum may be precipitated. The precipitate is most likely a lithium aluminum silicate isomorphous with β-quartz. Also, he concludes that visible color center phenomenon in quartz is related to substitutional aluminum impurity but not to interstitial aluminum.

The alkali elements, compensating for the valence defficiency of the substituting aluminum, are present in the concentration range of 3 to approximately 100 ppm. Up to 200 ppm lithium has been reported for quartz from a pegmatite containing lithium minerals (Stavrov 1961). However, due to the erratic precision of determinations, the stochiometric relations of lithium and sodium with aluminum or other cations can not be established.

Infrared absorption studies have established the presence of (OH) in quartz. Since the OH^- radical has about the same radius as O^{-2} ions, it is assumed that it would substitute for oxygen. In doing so, the $(OH)^-$ radical provides a valence compensation for aluminum and other trivalent cations. The content of $(OH)^-$, which seems to vary in successive growth zones of the crystal, is not known.

Another significant minor element in quartz of some igneous rocks is magnesium. However, it generally is present only in amounts of 1 ppm or less. Magnesium generally goes into six-coordination with oxygen, and this element may enter substitutional solid solution in

quartz in interstitial positions rather than in substitution for Si in four-coordination. There has been observed in low-quartz, which was formed by inversion from high-quartz solid solutions, the coupled solid solution of Mg and Al amounting up to 8% $MgAl_2O_4$. The Mn and Fe content in colorless quartz is relatively small, 1 ppm or less, although variable. The manner in which they are contained is not known. Rb, Cs, Ca, Ba, Pb, Ag, Sn, Cu, Zn, U, Cr, Zr, and V have been found in relatively small amounts or in traces in quartz. Whether these elements are present in solid solution or as impurities representing solutions entrapped in cavities or solid inclusions is not known.

III. EXPERIMENTAL PROCEDURE

A. Chemical Analysis

In this study, twenty-four samples of crystalline quartz were analyzed for their minor element content. Table I gives the location and description of each of the samples used. The quartz samples were prepared for analysis first, by washing with aqua regia, to remove surface contamination. Then they were heated to 800°C for ten minutes and quenched in distilled water at 25°C. By doing this the samples were broken down and their grinding was greatly facilitated. After drying in an oven, pieces were picked from the center of the samples to further guard against surface contamination. These pieces were then ground to minus 200 mesh in an agate mortar.

The spectrochemical analysis of the quartz specimens were made using the Bausch and Lomb Dual Grating Spectrograph with Applied Research Laboratories, Multi-source Unit, Model A 11,700. Table II lists the conditions found to be suitable for analysis of the samples. The photographic plates used for the analyses were Kodak SA#3 plates. The exposed plates were developed with Kodak D-19 developer under the following conditions: developer - 3½ minutes, stop - 30 seconds, fixer - 8 minutes, wash - 30 minutes. The above procedure was carried out at 25°C.

Strontium carbonate and tim oxide were used as internal standards. It was found that a mixture of powders in the ratio of 28 grams graphite: 1.2 grams $SrCO_3$: 0.3 grams SnO_2 provided the

Table I. Sample Description and Locality

Sample No.	Locality	Description
J-1	Streigag, Silesia	Crystal
J-2	White Plains, Alexander Co.,N.C.	Crystal
J-3	Hot Springs, Arkansas	Cubes cut from crystal
J-4	Herkimer Co., New York	Crystal
J-5	Moneta, Virginia	Crystalline Mass
J-6	Lincoln Co., North Carolina	Crystal Intergrowth
J-7	Albany, Maine	Crystalline Mass
J-8	Mt. Omel, Tzechnen, China	Crystal
J-9	Placerville, California	Crystal
J-10	Pincusion Peak, California	Crystalline Mass
J-11	Chimney Rock, California	Crystalline Mass
J-12	Crystal Peak, California	Crystalline Mass
J-13	White Rock Creek, California	Crystal
J-14	Madagascar	Crystalline Mass
J-15	Unknown	Crystal
J-17	Green River, Wyoming	Crystalline Mass
J-18	Brejauba, Minas Geraes, Brazil	Crystal
J-19	Corintho, Minas Geraes, Brazil	Crystal
J-20	Hot Springs, Arkansas	Crystal

Table I. (Continued)

Sample No.	Locality	Description
J-22	Cactus Mine, Utah	Intergrown Crystals
J-25	Rodrico Silva, Brazil	Crystal
J-26	Albany, Maine	Crystal
J-27	Murfrisboro, Arkansas	Crystal
J-28	Arkansas	Crystal

Table II. Conditions for Spectrograph

	Quartz Samples	Iron Rods
Conductance	Low Voltage-Interrupted	Low Voltage-Interrupted
Voltage	250 volts	250 volts
Current	-	-
Resistance	40 Ohms	-
Inductance	360	360
Capacitance	50	20
Filter No.	3	1
Transmission	100%	100%
Wavelength	2550-3530 Å	2550-3530 Å
	3850-4850 Å	3850-4850 Å
Time	10 Seconds	5 Seconds

best constancy of intensity of the lines corresponding to Sr and Sn. To obtain a complete and even burning of the quartz powders, a mix of 2.5 grams of graphite and internal standard mix and 2.0 grams of quartz powder was used. A homogeneous mix was obtained by grinding graphite mix and quartz powder under alcohol in an agate mortar. The alcohol was then allowed to evaporate. The resulting mixture was then packed into the craters, 3/16" deep and 1/4" diameter, of spectrographically pure graphite electrodes.

The chemicals used for standards were Johnson Matthey and Co. Spectrographically Standardized Substances except for $LiCO_3$, TiO_2, Cr_2O_3 and Ag_2O, which were Baker Analyzed Reagents (99.7% pure). A base mixture of standards plus silica was made up which contained one-tenth of a percent of the following elements: Al, Li, Na, K, Fe, Ti, Mg, Ca, Cr, Cu, Ge and Ag. The dilution scheme used is illustrated in Table III.

To construct the calibration curves for the two wavelength regions used in this analysis, the method described by Harvey (1950) was employed. First, a preliminary curve is constructed by plotting data as clear filter transmission versus absorbed step transmission. In this case, the data was obtained from iron lines of differing densities. The clear transmission of a particular line is measured, then the corresponding absorbed step transmission of the same line is measured. Thus data is obtained which may be plotted as mentioned above. The percentage of light absorbed (30%) need not be known for

Table III. Dilution Scheme for Standard Mixes

Mix	Weight of Mix (Grams)	Weight of SiO_2 (Grams)	Total Weight (Grams)	Weight of element in total weight ($\times 10^{-3}$ Grams)	% of element	ppm of element
A	2.5*	-	-	2.5	0.1	1000
B	0.5 of A	0.5	1.0	0.5	0.05	500
C	0.2 of A	0.4	0.6	0.2	0.0333	333
D	0.5 of B	0.5	1.0	0.25	0.0250	250
E	0.1 of A	0.45	0.55	0.1	0.0182	182
F	0.1 of D	0.10	0.20	0.025	0.0125	125
G	0.1 of F	0.10	0.20	0.0125	0.00625	62.5
H	0.1 of G	0.10	0.20	0.00625	0.003125	31.25
I	0.1 of H	0.10	0.20	0.003125	0.001563	15.63
J	0.05 of I	0.45	0.50	0.00078	0.000156	1.56

*To obtain Mix A, the compounds, which contain the elements to be determined, were weighed out according to the gravimetric factor of the element in the particular compound. Then, SiO_2 was added to bring the mix to 2.5 grams.

this step of the procedure, but is needed for the next step. Figures 1 & 2 are the preliminary curves for the regions 2550-3530Å and 3850-4850Å respectively.

The data from the preliminary curves is now transferred to an intensity (I) versus transmission (density) plot which is constructed on 2 cycle log/log graph paper. This is accomplished by arbitrarily selecting some clear step transmission value, from the preliminary curve, and giving it a value of I = 1.0. The corresponding absorbed step transmission value is then assigned a value of I = 0.3 (the step filter used had an absorption value of 30%). For example, to construct the curve in Figure 3, a clear transmission value of 50% from Figure 1 was selected as I = 1.0. Consequently, the absorbed transmission value of 23% is plotted as I = 0.3. Then, 23% of clear transmission is selected as I = 1.0, etc. To go in the opposite direction, 50% absorbed transmission is selected as I = 0.3 and, therefore, 76% clear transmission has I = 1.0. Figure 4 is the calibration curve for the region 3850-4820 Å.

Few points are thus obtained when a preliminary curve is used, but the validity of the points has been well established since any random scatter has already been compensated for in drawing the preliminary curve. An advantage in using this method is that the intensities of the iron lines used need not be known.

To construct the working curve for a particular element, the density of the line corresponding to the particular element and the density of the line corresponding to the internal standard is obtained.

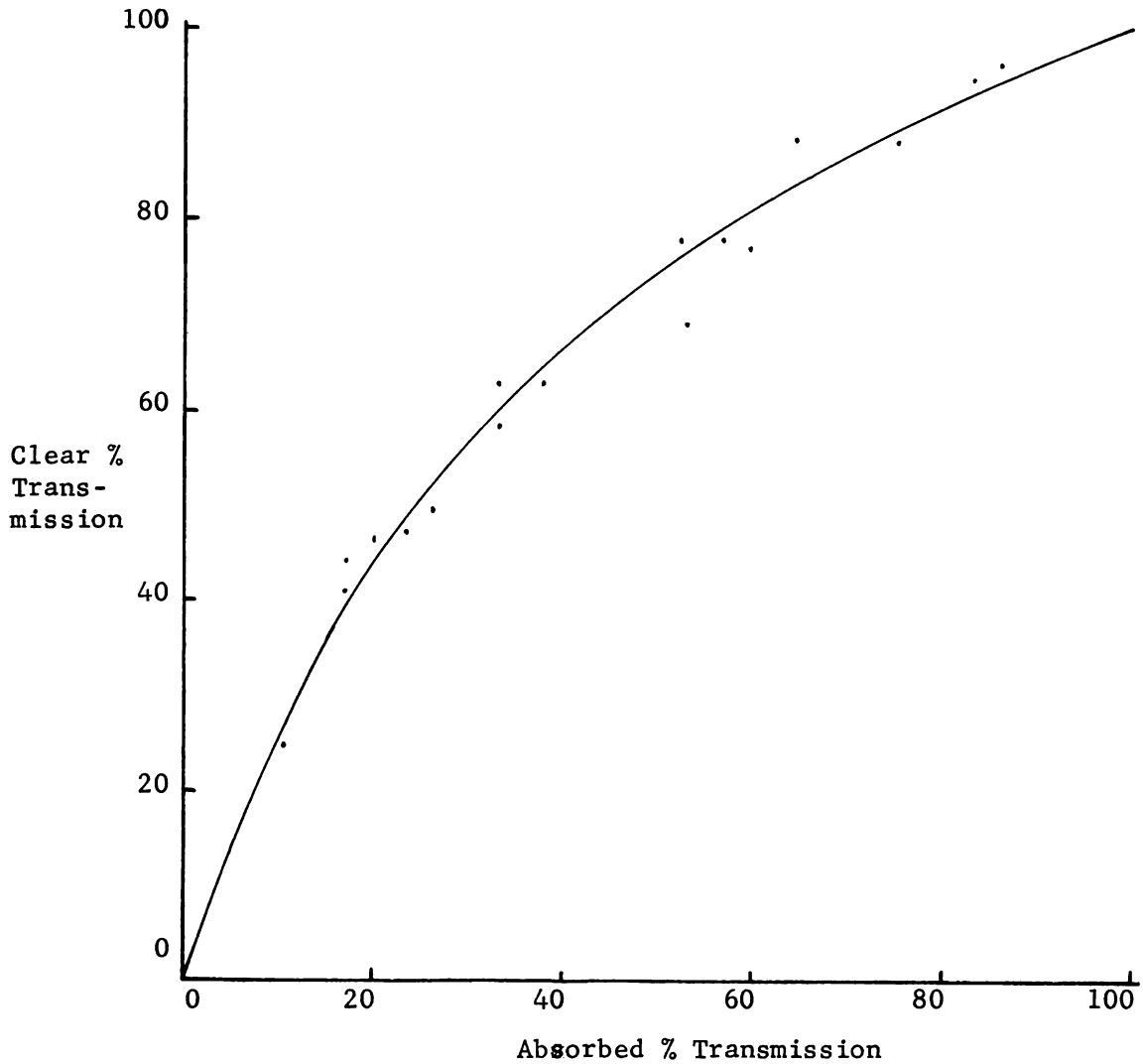


Fig. 1 Clear % T v/s Absorbed % T for the Region 2550-3530Å.

Fig. 3 Calibration Curve for the Region 2550-3530Å.

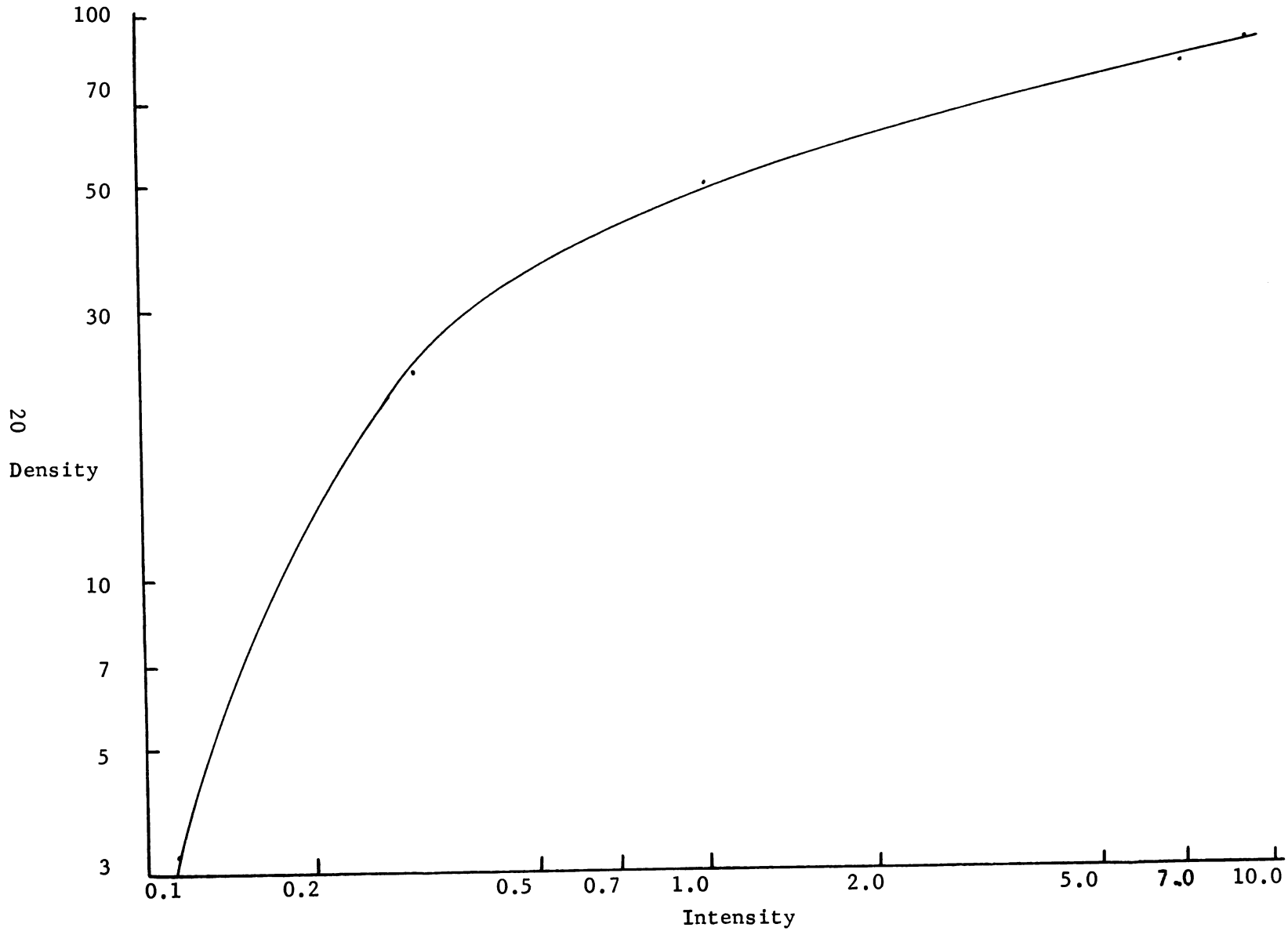
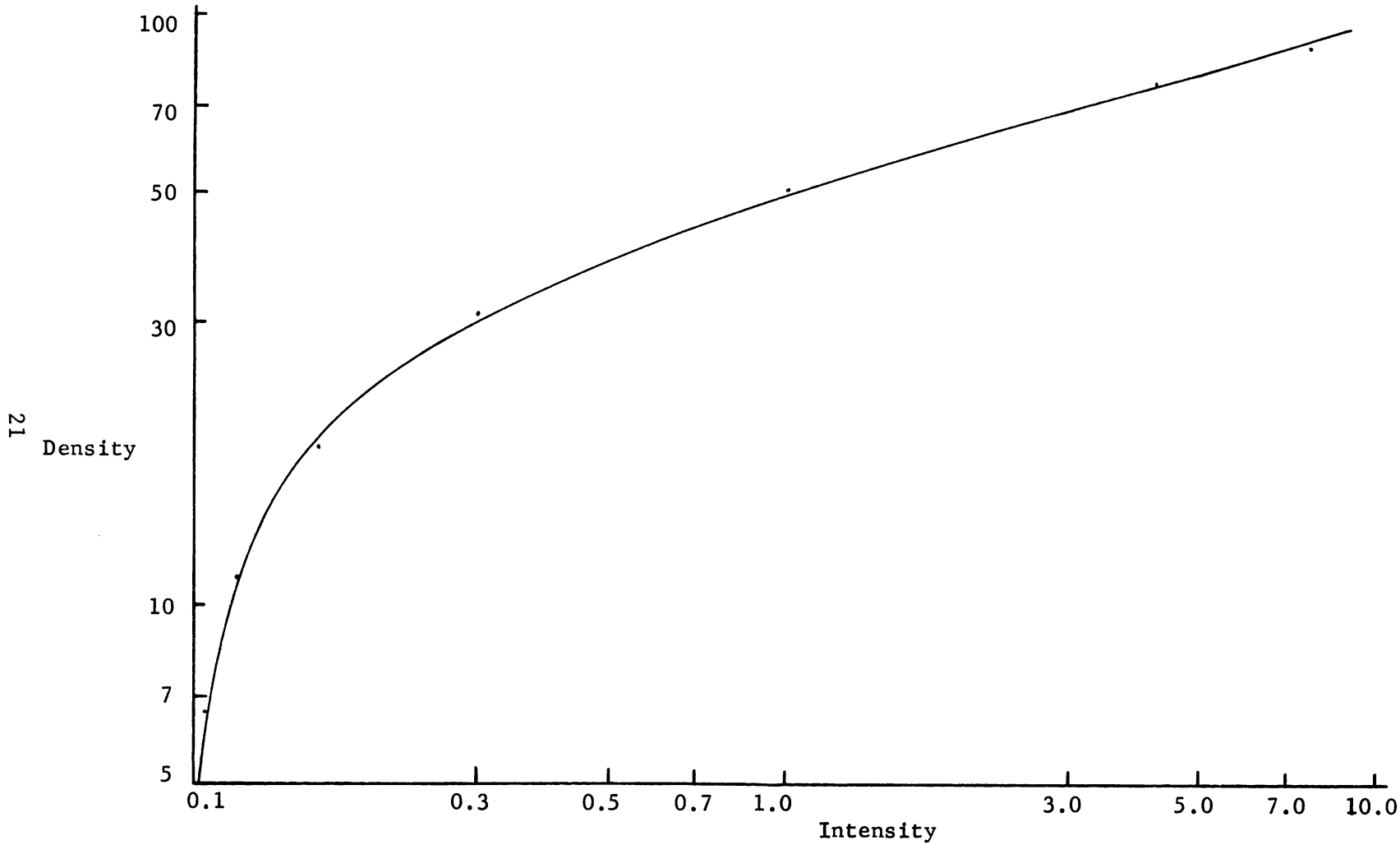


Fig. 4 Calibration Curve for Region 3850-4850Å.



These densities are then converted to intensities by means of the calibration curve. Then, the ratio of the intensity of the particular element line to the intensity of the internal standard line is plotted against the concentration of the particular element. The plotting is done on 2 cycle log/log graph paper. The three points for each concentration value corresponds to the three samples of each standard mix which were run in order to provide a reproducibility check. Figures 5, 6, 7, 8, 9, 10, 11 and 12 are the working curves for Al, Fe, Ti, Mg, Ca, Cr, Cu and Ag respectively. Table IV lists the particular line used for the analysis of each element. A working curve was not constructed for Ge, since it was not detected in any of the samples. The density readings were made on the Jarrell-Ash "Recording Microphotometer", Model No. JA-203.

The accuracy of the analyses ranged from 1.5 - 5.2%. The precision ranged from 3.1 - 6.6%. The error due to microphotometric readings is approximately 1 - 2%.

B. X-Ray Analysis

The measurements of the unit cell dimensions of the quartz samples were made on powders using a General Electric XRD-5 diffraction unit. The following conditions were used: CuK_{α} radiation, scanning speed of 2^{o} per minute, time constant of 4 seconds, slit width of 1^{o}, collimating slit of 0.2^{o}, 50 Kv voltage, 16 ma amperage and a double nickel foil filter.

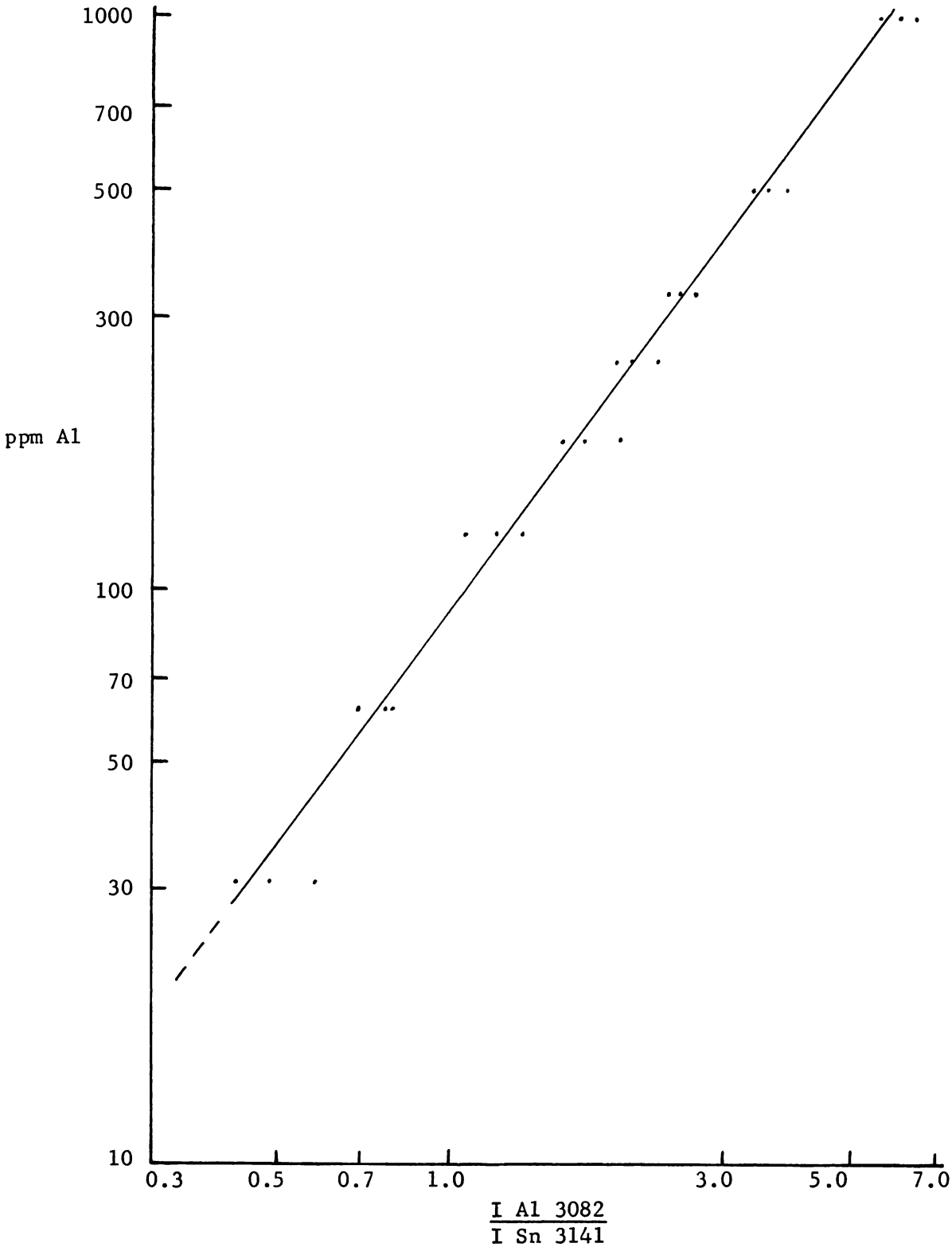


Fig. 5 Working Curve for Aluminum

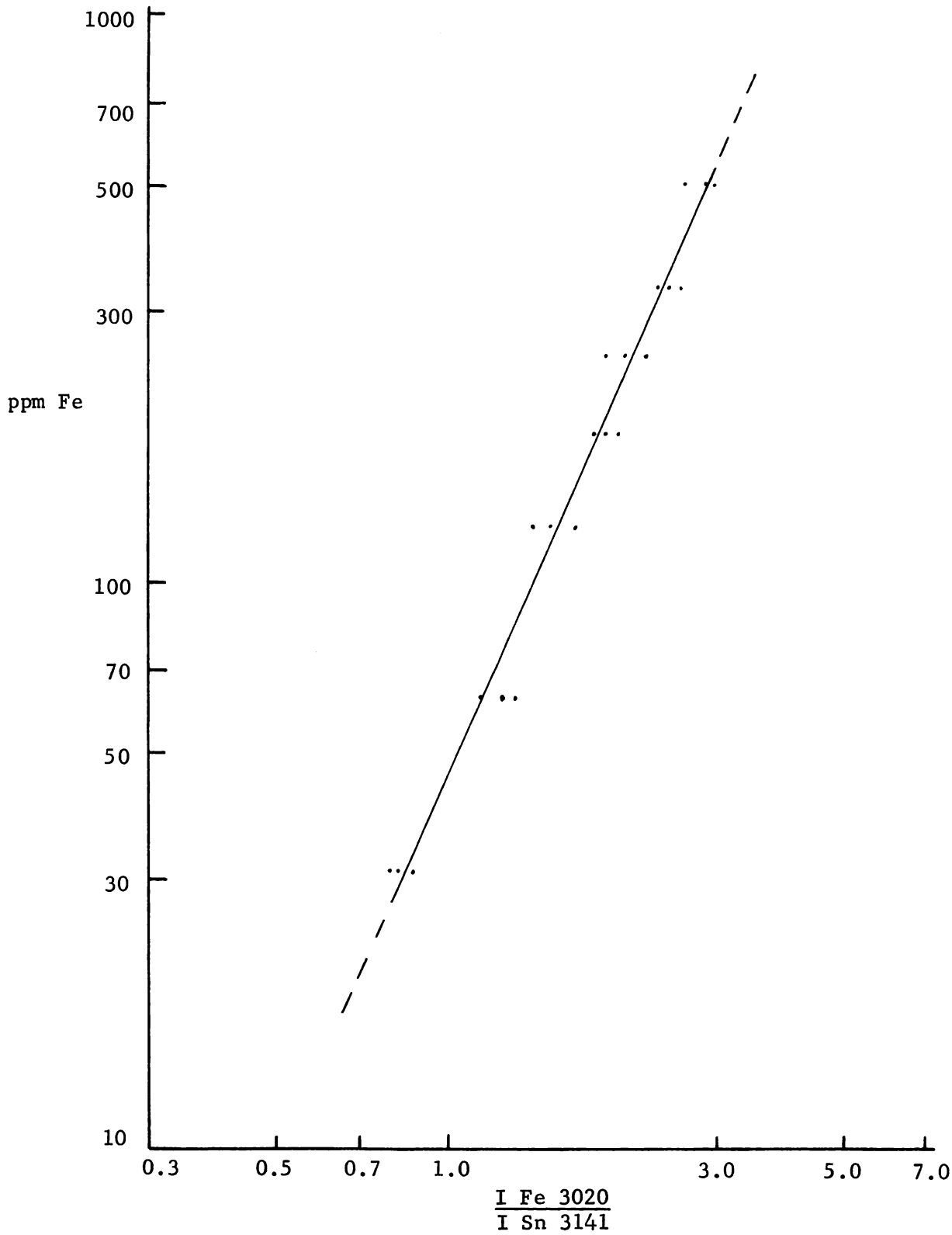


Fig. 6 Working Curve for Iron

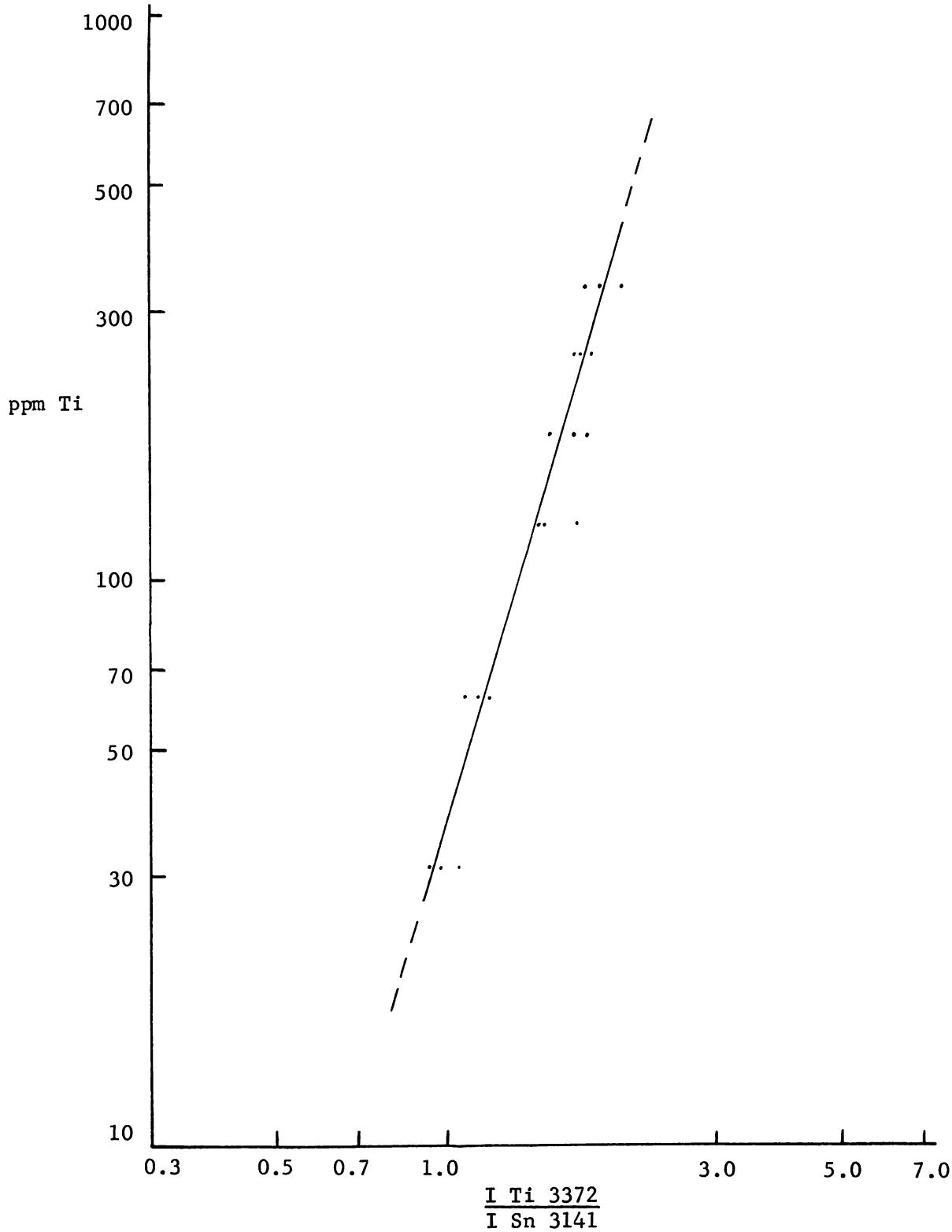


Fig. 7 Working Curve for Titanium

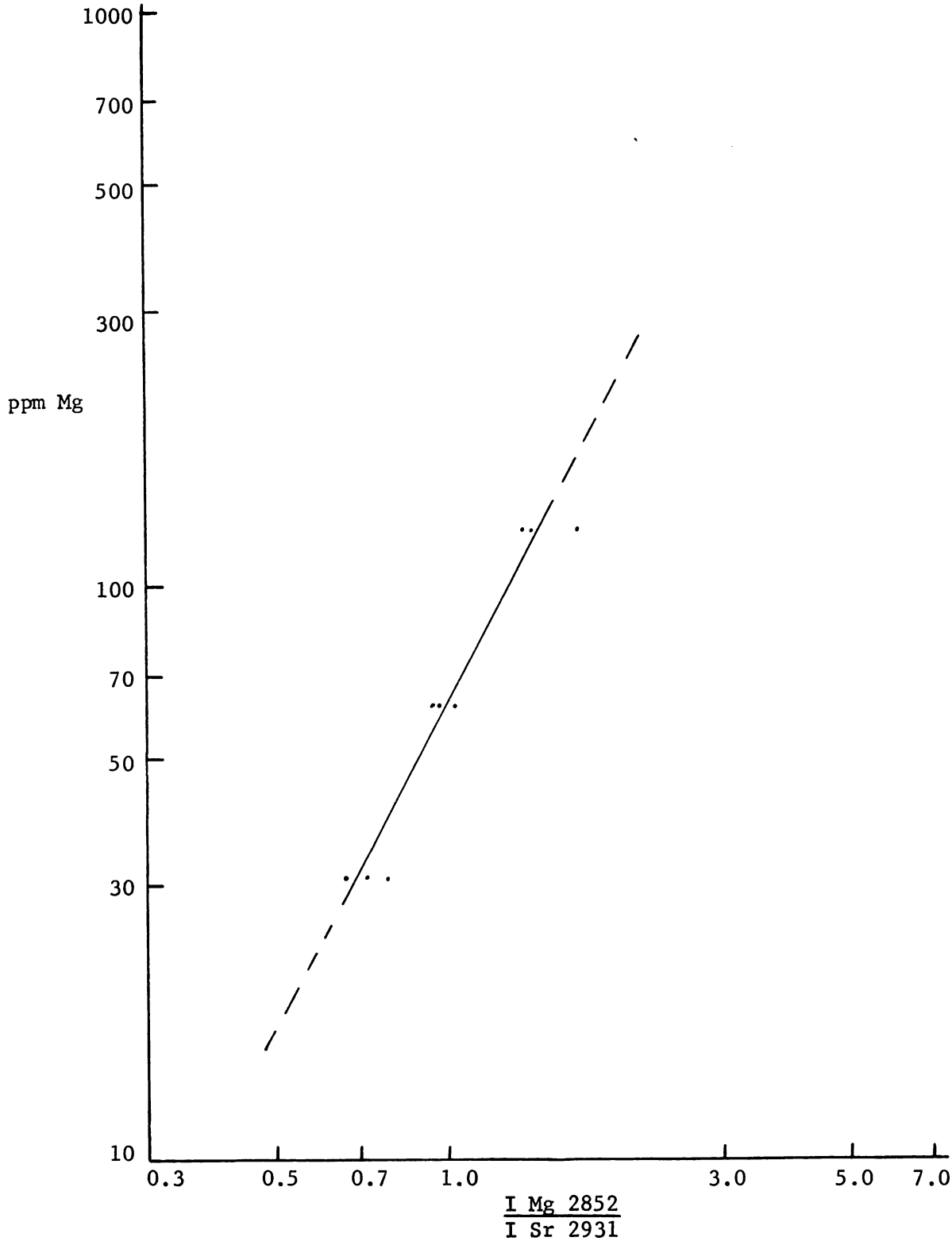


Fig. 8 Working Curve for Magnesium

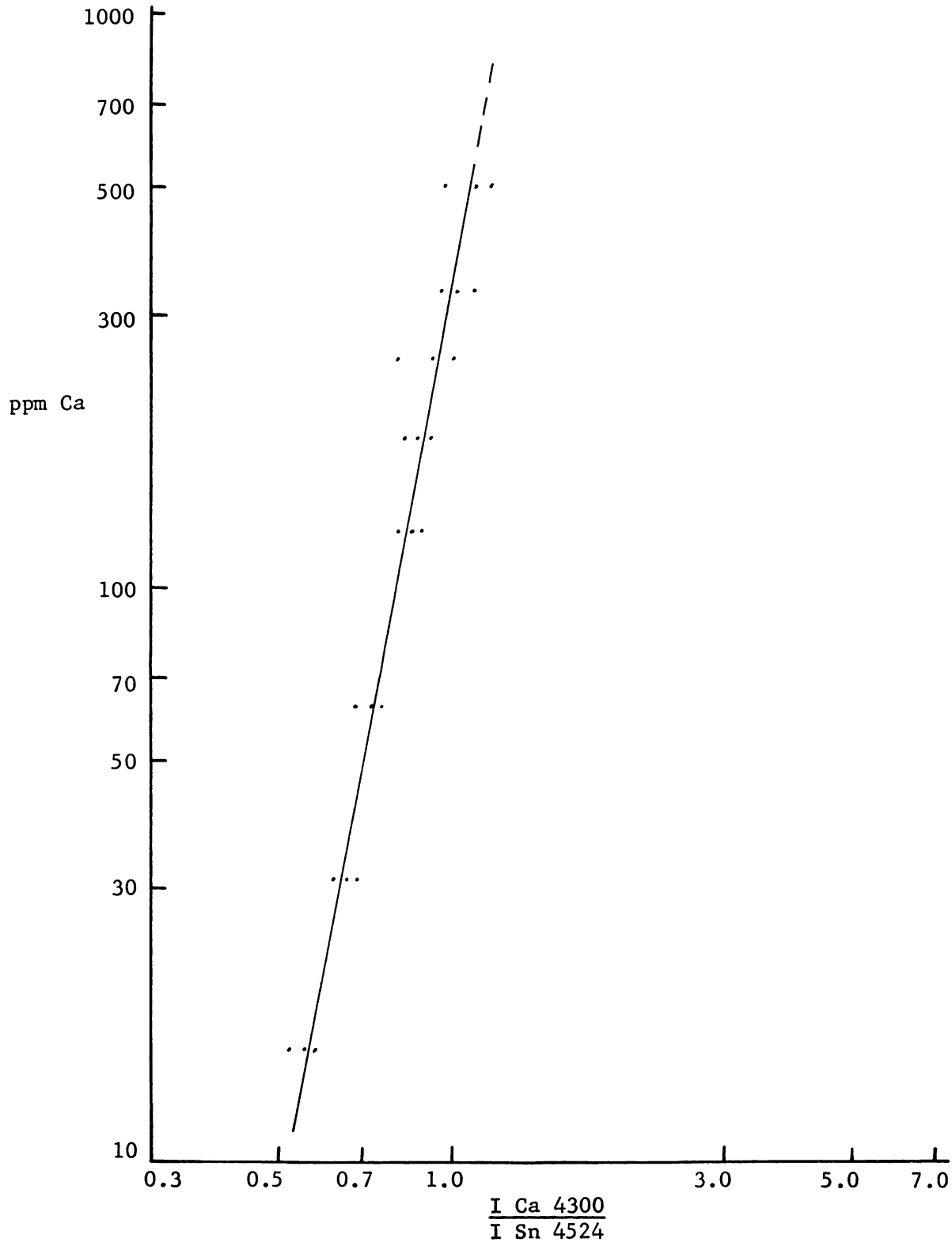


Fig. 9 Working Curve for Calcium

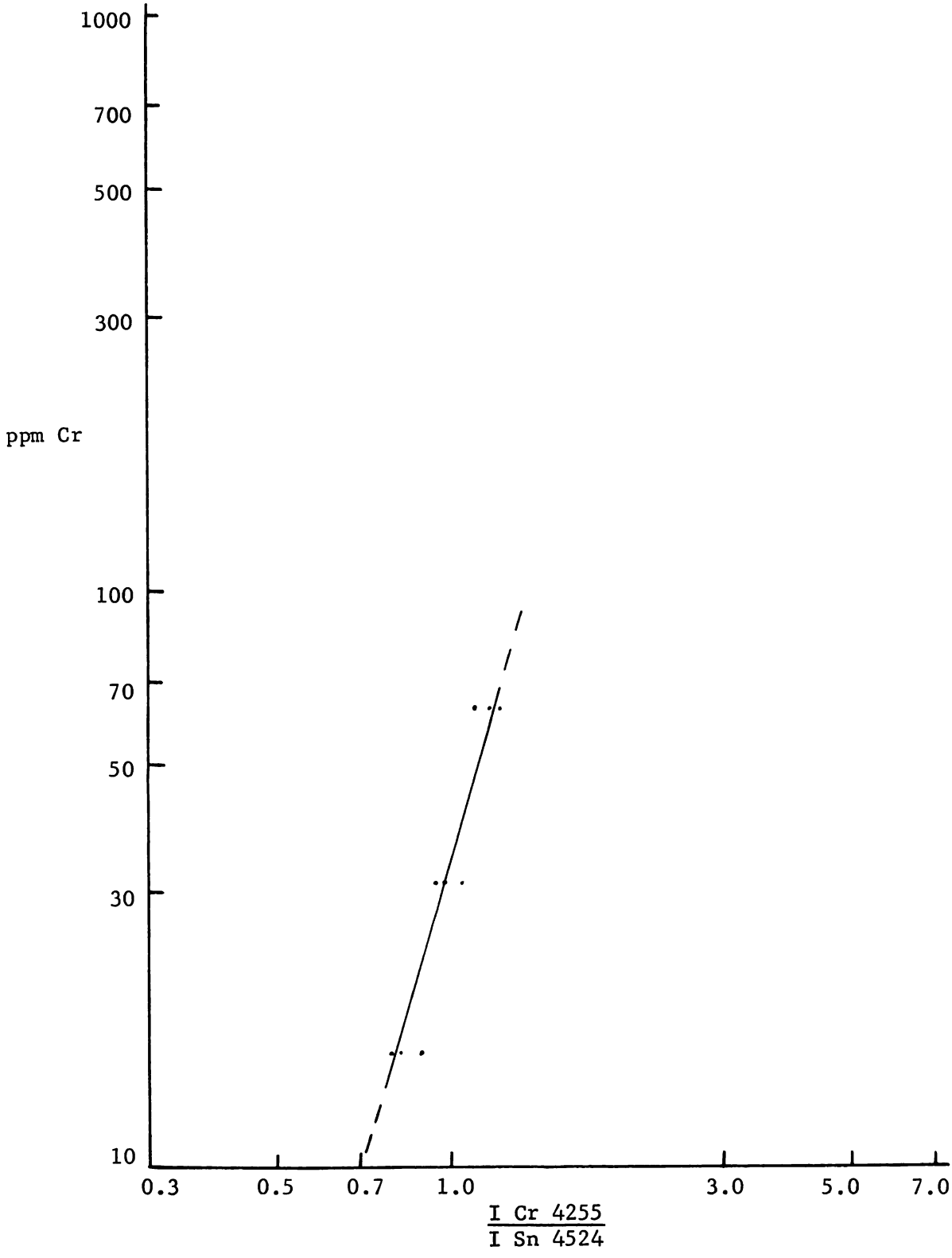


Fig. 10 Working Curve for Chromium

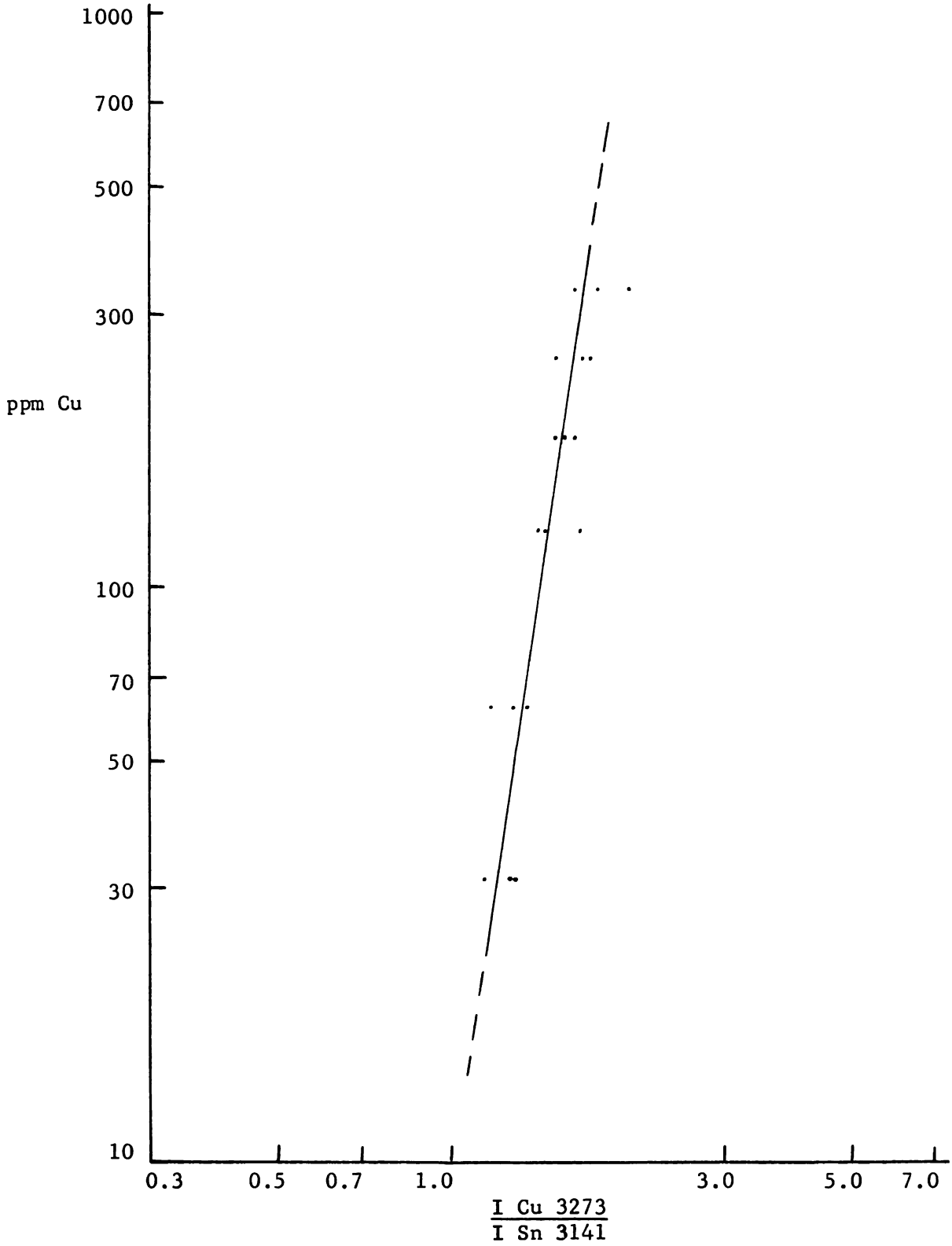


Fig. 11 Working Curve for Copper

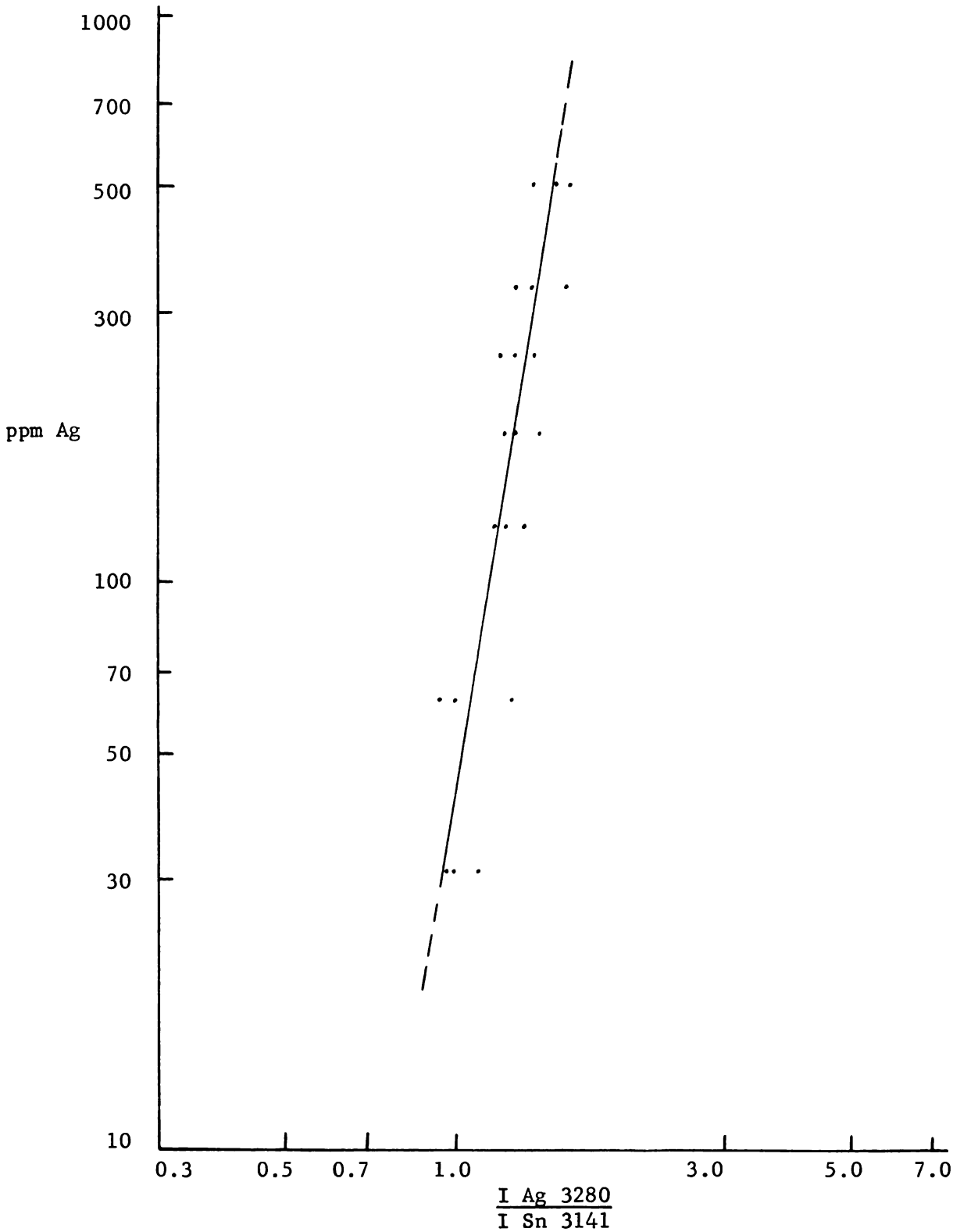


Fig. 12 Working Curve for Silver

Table IV. Spectrochemical Data: Element Sought, Wavelength of Spectral Line Used and Minimum Sensitivity Attained

Element	Line Used	Detection Limit
Aluminum	3082Å	30 ppm
Iron	3020Å	30 ppm
Titanium	3372Å	30 ppm
Magnesium	2852Å	30 ppm
Calcium	4300Å	15 ppm
Chromium	4255Å	15 ppm
Copper	3273Å	30 ppm
Silver	3280Å	30 ppm

Angular values of 2θ read to the nearest 0.01° were obtained, by mannual scanning, for the peaks which represent the following crystallographic planes: 331, 420, 315, 421, 324 and 216. These peaks which occur in the 2θ region, 143° to 159°, are sharp, well defined and of high intensity. In this high angle region, the doublets are well resolved, thereby minimizing any error due to misidentification. Corresponding "d" values for the measured reflections were obtained from the Tables of Interplanar Spacings For Angle 2θ contained in the instruction manual for the above mentioned diffraction unit.

The unit cell dimensions of each sample of quartz were calculated from the measured interplanar spacings using the least -squares scheme outlined below.

From the equation

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + k^2 + hk)}{a^2} + \frac{l^2}{c^2}$$

where d interplanar spacing; h,k,l,= Miller indices and a and c are the cell edges, the equation

$$z = x\alpha + y\beta \qquad (1)$$

was obtained in which $z = 1/d^2$, $\alpha = 1/a^2$, $\beta = 1/c^2$, $x = 4/3(h^2+k^2+hk)$ and $y = l^2$.

Multiplying eq. 1 first by x and then by y and then rearranging, equations 2 and 3 result.

$$\alpha x^2 + \beta xy - xz = 0 \qquad (2)$$

$$\alpha xy + \beta y^2 - yz = 0 \qquad (3)$$

Therefore, for a series of measurements,

$$\alpha \sum_i x_i^2 + \beta \sum_i x_i y_i - \sum_i x_i z_i = 0 \qquad (4)$$

and

$$\alpha \sum_i x_i y_i + \beta \sum_i y_i^2 - \sum_i y_i z_i = 0 \qquad (5)$$

Values for equations 4 and 5 were obtained for each set of data, that is, the interplanar spacings corresponding to 331, 420, 315, 421, 324 and 216 for each sample. Then the equations were solved simultaneously for α and β, from which a_o and c_o could be determined quite easily.

Two factors contribute to the error involved in the x-ray analysis: sample preparation and the measurement of 2θ. In calibrating the diffraction unit with a novaculite plate, it was found that within the region 143^o to 159^o, the peak positions could be reproduced, on an average, to within $\pm 0.03^o$. The error due to sample preparation may be attributed to the differences in the thickness of the powdered sample from slide to slide. The error was checked by making five slides of one sample, taking their x-ray diffraction patterns and measuring the peaks used above. The change in peak position in relation to the original sample were then computed and an average value obtained. This value was $\pm 0.03^o$. Combining this value with that above, a maximum error is obtained due to both factors, that is, $\pm 0.06^o$. In terms of unit cell dimensions, this error in the 2θ value produces an error of ± 0.0007Å in a_o and an error of ± 0.0008Å in c_o.

IV. RESULTS AND DISCUSSION

The twenty-four samples of quartz studied showed a wide range of impurity content and unit cell dimensions (Tables 5 and 6). Aluminum, with a concentration range of 120-550 ppm, is the major impurity in quartz. Magnesium has a range of less than 10 to 63 ppm; titanium ranges from less than 10 to 42 ppm; calcium ranges from less than 10 to 55 ppm; iron ranges from less than 10 to 50 ppm and chromium ranges from less than 10 to 20 ppm. The least abundant impurity ions are copper and silver. Copper is presnet in the amount of less than 10 to 21 ppm and silver content is less than 10 ppm for all samples. Both copper and silver may be present in inclusions.

That aluminum is the major impurity ion in quartz may be explained to its similarity to silicon. The small size of the silicon ion rules out extensive substitution by quadrivalent ions such as titanium, zirconium, tin, thorium and uranium. (Table 7 lists the ionic radii of some of the elements of interest.) All of these ions are considerably larger in size than silicon and generally go into higher coordination with oxygen. Titanium, the smallest of these ions, is present in limited amounts in colorless quartz, as reported above. The presence of titanium may be due to the inclusion of minute crystals of rutile, TiO_2. The higher polymorphs of α-quartz may contain titanium in larger amounts. In stishovite, where silicon is in six-fold coordination with oxygen, we might expect the largest amount of titanium substitution. However, since stishovite is formed from preexisting quartz by means of shock, the titanium content would be that of the original quartz.

Table 5. Impurity Content in Quartz

Sample No.	Concentration (ppm)							
	Al	Fe	Ti	Mg	Cr	Ca	Cu	Ag
J-1	123	44	<10	33	20	21	<10	<10
J-2	127	28	<10	60	nd	10	<10	<10
J-3	120	44	<10	34	nd	<10	<10	<10
J-4	510	32	<10	63	<10	<10	<10	<10
J-5	300	29	<10	10	<10	55	<10	<10
J-6	295	44	17	48	17	<10	<10	<10
J-7	420	29	17	12	<10	16	<10	<10
J-8	295	45	20	34	<10	21	<10	<10
J-9	415	35	<10	10	16	15	21	<10
J-10	420	36	42	32	<10	10	16	<10
J-11	310	32	25	20	<10	26	16	<10
J-12	400	48	21	24	<10	13	11	<10
J-13	170	31	21	27	<10	<10	11	<10
J-14	345	33	18	22	<10	12	11	<10
J-15	380	35	37	30	<10	10	14	<10
J-17	370	44	33	49	<10	12	10	<10
J-18	200	<10	<10	<10	<10	12	<10	<10
J-19	500	<10	<10	<10	<10	<10	<10	<10
J-20	550	31	10	17	<10	10	<10	<10

Table 5. (Continued)

Sample No.	Concentration (ppm)							
	Al	Fe	Ti	Mg	Cr	Ca	Cu	Ag
J-22	385	15	<10	<10	<10	23	<10	<10
J-25	250	<10	<10	23	<10	<10	<10	<10
J-26	420	30	<10	31	<10	<10	<10	<10
J-27	280	50	12	33	<10	<10	<10	<10
J-28	370	40	13	29	<10	<10	<10	<10

Table 6. Unit Cell Dimensions, Axial Ratios and "Increment Ratios" of Quartz

Sample No.	a_o	c_o	c/a	$\Delta a/a/\Delta c/c$
J-1	4.9064	5.3994	1.1005	1.4444
J-2	4.9081	5.3994	1.1001	1.1111
J-3	4.9093	5.3947	1.0989	0.3889
J-4	4.9075	5.3932	1.0990	0.5238
J-5	4.9058	5.3986	1.1005	1.2727
J-6	4.9087	5.4017	1.1004	1.8000
J-7	4.9087	5.3963	1.0993	0.6000
J-8	4.9087	5.3978	1.0996	0.7500
J-9	4.9064	5.4010	1.1008	2.1667
J-10	4.9081	5.3986	1.0999	0.9091
J-11	4.9070	5.3994	1.1003	1.3333
J-12	4.9075	5.3994	1.1002	1.2222
J-13	4.9087	5.3986	1.0998	0.8182
J-14	4.9075	5.3978	1.0999	0.9167
J-15	4.9093	5.4017	1.1003	1.4000
J-17	4.9075	5.3994	1.1002	1.2222
J-18	4.9093	5.4002	1.1000	0.8750
J-19	4.9070	5.4025	1.1010	3.0000
J-20	4.9093	5.4010	1.0002	1.1667

Table 6. (Continued)

Sample No.	a_o	c_o	c/a	$\Delta a/a/\Delta c/c$
J-22	4.9075	5.4017	1.1007	2.2000
J-25	4.9070	5.3978	1.1000	1.0000
J-26	4.9081	5.4017	1.1006	2.0000
J-27	4.9087	5.4010	1.1003	1.5000
J-28	4.9081	5.4002	1.1003	1.2500

Table 7. Ionic Radii of Elements
(After Pauling, 1960)

Ion	Crystal Radii (Å)
Si^{+4}	0.41
Al^{+3}	0.50
Ge^{+4}	0.53
Ti^{+4}	0.68
Zr	0.80
Su^{+4}	0.71
Th	1.02
U	0.97
Mg^{+2}	0.65
Ca^{+2}	0.99
Cr^{+3}	0.52
Fe^{+3}	0.64

Another quadrivalent ion close in ionic size to silicon (0.41Å) is germanium (0.53Å). Since germanium has a similar ionic radius to that of silicon and has the same charge as silicon, an extensive substitution of germanium for silicon might be expected. Germanium has been introduced into solid solution is synthetic quartz up to amounts in the range of 0.3% (Stanley and Theokritoff, 1956; Frondel and Hurlbut, 1955). However, it has been found to be lacking in the natural quartzes analyzed in this study. The factors contributing to the scarcity of germanium in quartz are (1) the great difference in crustal abundance between silicon (277,200 ppm) and germanium (2 ppm) and (2) the relatively high solubility of germanium compounds.

As was mentioned above, aluminum is the major impurity ion in quartz. This is due to the similarities between the silicon ion and the aluminum ion: (1) the ionic radii are similar, Si^{+4} = 0.41Å and Al^{+3} = 0.50Å and (2) the two ions are isoelectronic. Two ions are isoelectronic when they have the same electronic configuration; either that of an inert gas in which the outer shell contains eight electrons, or that of a psuedo-inert gas structure in which the outer shell contains eighteen electrons. Another similarity is that the radius ratio of each of these elements to oxygen, Si/O = 0.292 and Al/O = 0.357, is within the range of values for tetrahedral coordination (0.225-0.414). Although the aluminum to oxygen ratio is close to the critical value for octahedral coordination, Al is found six-coordinated in silicate minerals, but may also substitute for

silicon in four-coordination. While the substitution of aluminum for silicon may be extensive in other silicates, it is rather limited in quartz. This is due to the limitations put on the opportunities for valence compensation of the trivalent ion by the simple composition and the relatively tight crystal structure of quartz.

The deficiency of valence brought about by the substitution of aluminum for silicon may be satisfied by either the coupled entrance of a small monovalent ion, sodium potassium and/or lithium, into interstitial positions or by the coupled substitution of (OH) for oxygen. As has been mentioned previously, OH^- has been found in quartz, however, the amounts present are not known. The concentrations of Li, K and Na were not determined in this study since the sensitivity of the infrared film used was not adequate to detect the maximum amount of these elements in the standards (1000 ppm). However, they should be present, theoretically, in the amounts equal to that of the aluminum and other trivalent ions present. The discrepancies that arise here may be due to defect structures, the presence of three interstitial aluminums for one substituted aluminum and the substitution of (OH) for oxygen.

The manner in which iron, calcium and chromium are contained in quartz is not known. Their presence in the samples analyzed may be due to solid inclusions or contaminations. The substitution of magnesium in interstitial positions in quartz has been discussed previously.

Table 6 shows that the unit cell dimensions of quarts are variable; a_o varies from 4.9058Å to 4.9093Å and c_o varies from 5.3932Å to 5.4025Å. This is a variation of one part in 10^3 for both parameters, which is consistant with the work of Keith and Tuttle (1952). The variation of lattice parameters and impurity content substantiate the conclusions of Keith and Tuttle (1952) and Keith (1955) concerning the dependence of the variation of lattice parameters on the presence of impurity ions. However, the manner in which the impurity ions affect the variation in lattice parameters has not been confirmed. In an attempt to clarify the manner of variation, the aluminum content of the quartz samples was plotted versus the unit cell dimensions, a_o and c_o (Figures 13 and 14). An examination of these plots shows that there is no relationship except that the unit cell dimensions do vary with impurity content.

Also, the cell parameters of the twenty-four quartz samples were compared to Keith's Brazilian quartz mentioned previously and the "increment ratios" and axial ratios were calculated (Table 6). A plot of the axial ratio versus the "increment ratio" (Figure 15) shows a correlation between them, that is, as the axial ratio increases so does the "increment ratio". This would seem to suggest that both cell parameters increase with impurity content, although unevenly. Using Cohen's rules, it was found that most of the samples contain substitutional impurities, the main impurity being

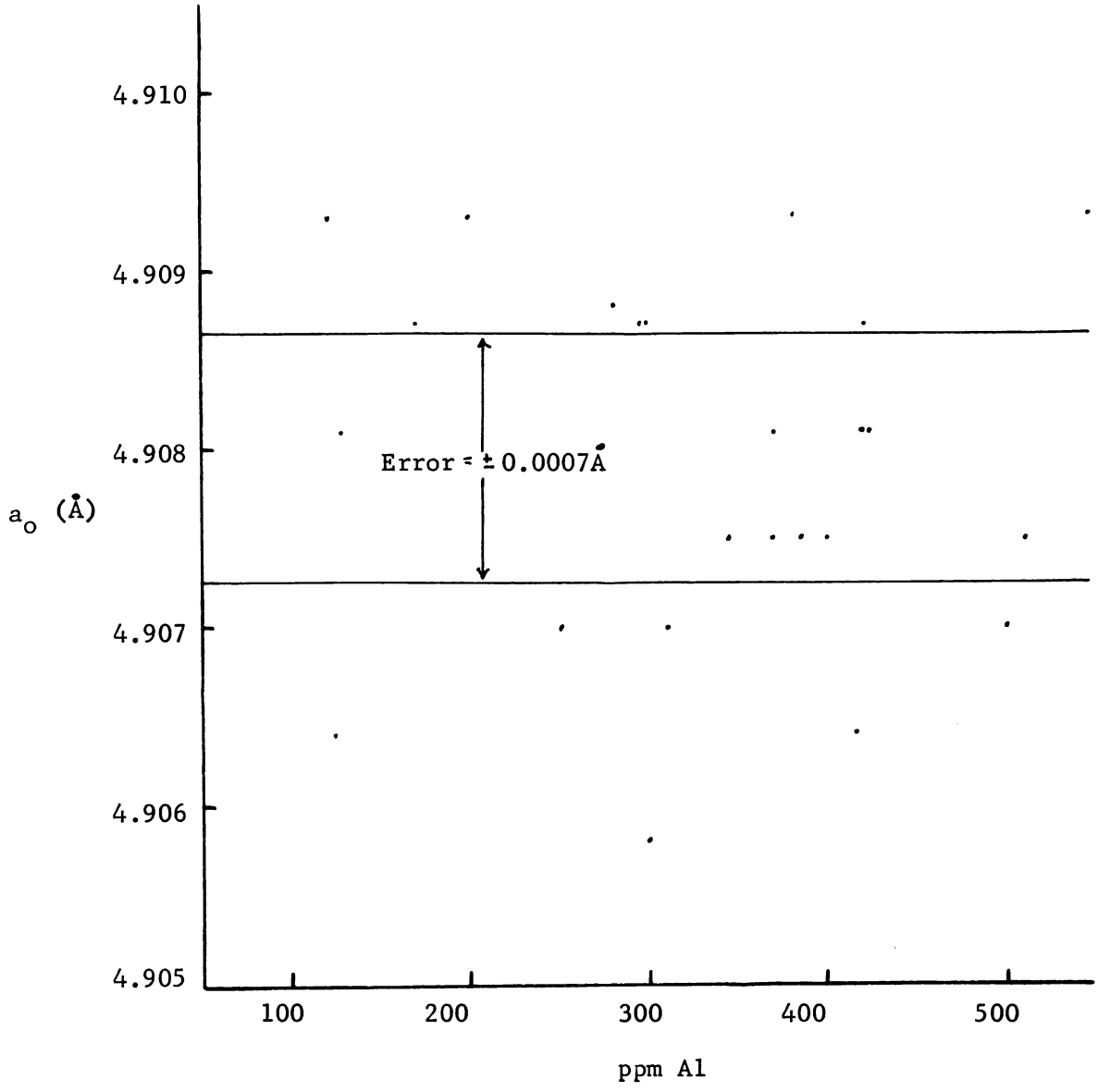


Fig. 13 Aluminum Content versus a_o.

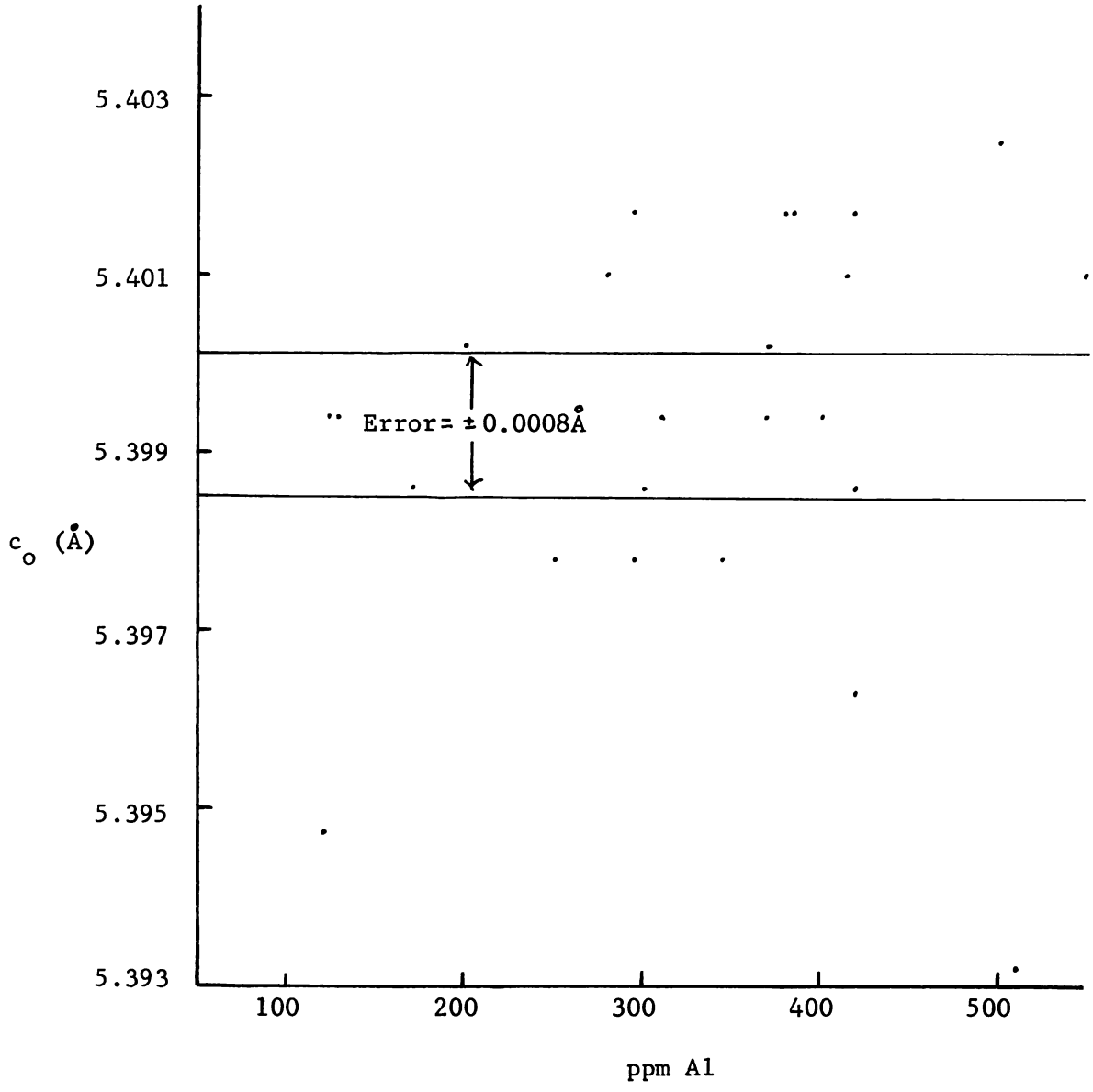


Fig. 14 Aluminum Content versus c_o.

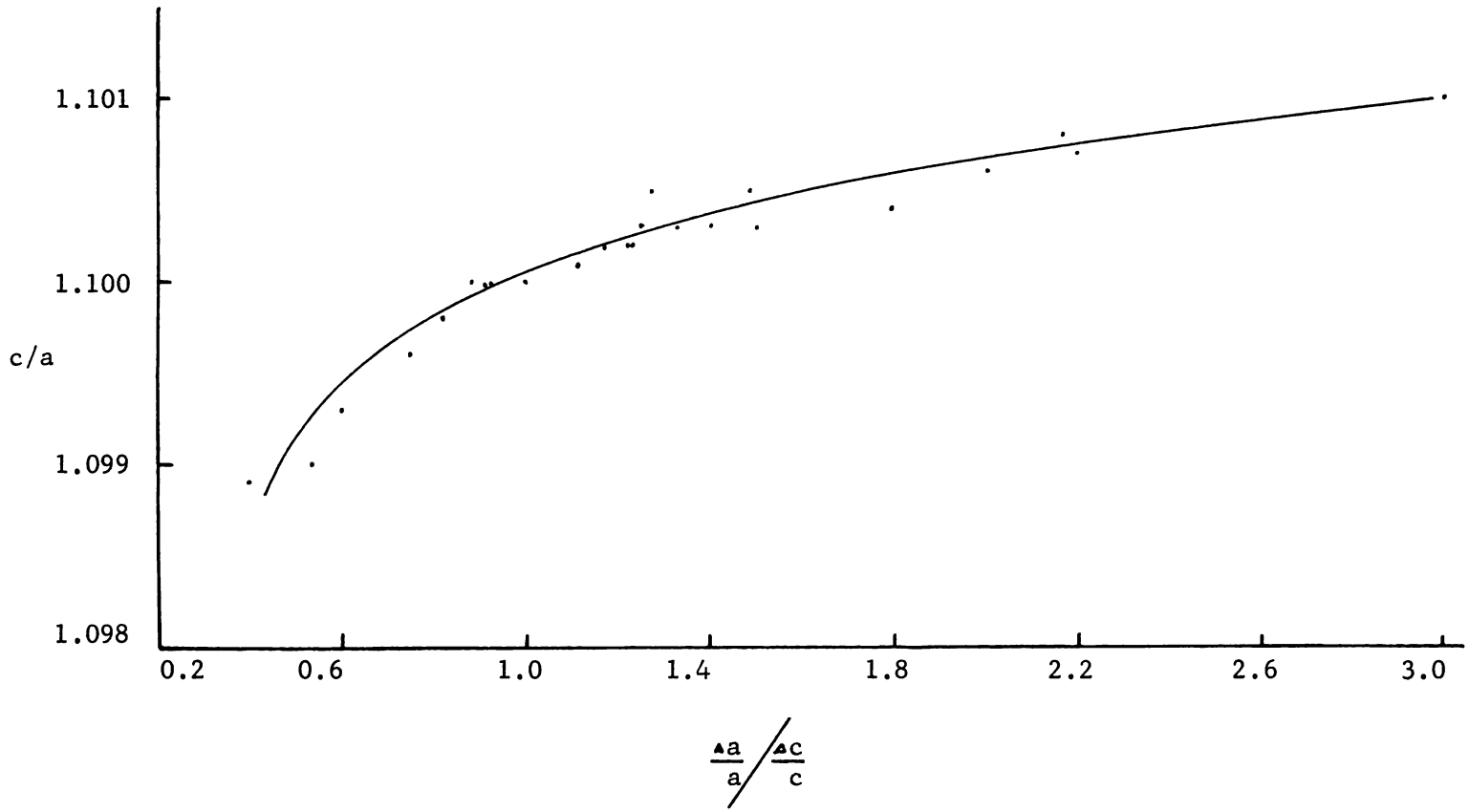


Fig. 15 Axial Ratio versus "Increment Ratio".

aluminum. Three samples, 1, 15 and 27, have an intermediate "increment ratio" and therefore contain both substitutional and interstitial impurities. A high percentage of interstitial impurities are present in samples 6, 9, 19, 22 and 26 since their "increment ratios" are greater than 1.7.

An examination of the axial ratios of the latter five samples show that they increase with increasing "increment ratios" and also with increasing aluminum content. This would seem to suggest that, although a_o is increasing more than c_o is increasing, indicating an increase in interstitial impurities, the increase in c_o indicated an increase in the amount of substitutional impurities. Therefore, it might be concluded that as the aluminum content increases, both the amount of substitutional and the amount of interstitial impurity increases proportionately.

If the axial ratios and increment ratios of samples 12, 17 and 20 are examined, it is found that the former ratios are equal and the latter ratios are essentially equal. However, their lattice parameters increase as the aluminum content increases. This also would suggest that the substitutional and interstitial impurities increase proportionately with increasing impurity content.

V. CONCLUSION

(1) Aluminum is the major impurity in natural, colorless quartz. Also present as impurities are Fe. Ti, Mg, Cr, Ca, Cu and Ag. These impurities may be either substitutional or interstitial. The substitution of aluminum for silicon seems reasonable in view of the fact that they have similar ionic radii and are isoelectronic.

(2) The unit cell dimensions of quartz show a wide range of variation and this variation is due to impurity content. A plot of the axial ratios and the "increment ratios" showed that one increased with the other, suggesting that as a_o increases c_o increases. This is attributed to the fact that both interstitial and substitutional impurities are present in quartz. However, substitutional impurities predominate in the greater majority of quartz.

(3) An examination of specific samples showed that an increase in a_o and c_o with increasing impurity content is caused by a proportional increase of substitutional and interstitial impurities.

VI. SUGGESTIONS FOR FURTHER RESEARCH

1. All the samples used in this study were of hydrothermal origin. Thus, it might be said that the curve in Figure 15 is indicative of quartz which grew at a certain temperature or within a certain temperature range. Therefore, a study of quartz which grew within different temperature ranges might produce curves of a different nature.

Also, the quartz samples used were colorless. Therefore, a study of other types of quartz, i.e. smoky, rose or amethyst, might also produce curves of a different nature than that in Figure 15.

2. Analysis of the precipitate obtained from colorless quartz on heat treatment and the clear portion to determine the amount of substitutional and interstitial impurities; aluminum and lithium and/or sodium.

3. The study of other minerals to determine the effects of impurities on unit cell dimensions and other properties.

4. A study of many more quartz samples to determine statistically the limits of substitution of impurities.

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