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ON THE CHEMISTRY AND COLOR OF AMETHYST

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ABSTRACT

The color of amethyst results from substitution of small quantities of ferric iron for silicon followed by irradiation. The overall trace-element content is not greatly different from colorless quartz, but stoichiometric calculations indicate that some or all of the iron present must be Fe^{3+} in tetrahedral coordination. Comparison of colorless and colored portions of the same crystals shows the iron content to increase both with respect to aluminum and in absolute amount from colorless to amethystine portions. Growth temperatures are calculated to be 70–285°C with a median of 250°C.

INTRODUCTION

The color of amethyst has been a matter of speculation for a very long time and has been ascribed to a wide range of contaminants including dispersed solids, hydrocarbons, titanium, and manganese. Work in the past decade, however, has shown that trivalent iron substituting for silicon is the responsible agent. Evidence for the implication of iron as the cause of the color of amethyst comes indirectly from its common association with iron minerals and directly from chemical analysis, absorption spectra, and electron paramagnetic resonance (EPR) studies. A summary, probably incomplete, of the various authors who have contributed to an understanding of the color of amethyst through 1964, when the role of iron-activated color-centers was conclusively demonstrated by Hutton (1964) and Barry & Moore (1964), is given in Table 1.

With the basis for the coloration understood, there remains the need to explain its geochemical milieu. Amethyst is typically found in cavities and druses in hydrothermal veins, pegmatites, basalts and other igneous rocks and in geodes where it is commonly associated with iron oxide, carbonate, or silicate minerals. Recognizable spherules of iron oxide are sometimes included within the crystals, and analysis indicates that the tiny black inclusions found in some crystals are iron-rich.

Chemical analyses reported by various authors show amethyst to contain significant amounts of iron, although not unusually more than ordinary uncolored quartz. Of considerable importance, however, is the increase in iron content with increased depth of color of the specimen as shown by Tsinober & Chentsova (1959), Chuboda (1962), and Konno (1967). The color changes which amethyst undergoes upon heating and irradiation are also suggestive of an iron-activated color center. These changes are from violet to gray-violet to clear to (sometimes) yellow to milky with increasing temperature, the yellow variety being identical with citrine. Heat-bleached material may be restored to its original color by *x*-irradiation (Berthelot 1906; Holden 1925).

TABLE 1. AUTHORS SUGGESTING IRON IN SOME FORM AS THE AGENT RESPONSIBLE FOR THE COLOR OF AMETHYSTINE QUARTZ

Author	*Date*	*Coloring Agent*
	Iron Compounds	
Haüy	1817	iron oxide
Marx	1831	hydrated iron oxide
Poggendorf	1841	iron acid
Heintz	1860	iron acid
Engler & Kneis	1887	ferric carbonate
Nabl	1889	$Fe(SCN)_3$
Hermann	1908	ferrous, ferric, and manganese compounds
Holden	1925	ferric compound
Vedeevna	1940	dispersed inclusions of elementary iron
	Dissolved atoms or ions	
Woodward	1729	"ferreous" molecules
Wild & Liesegang	1923	dissolved ions or atoms
Hoffman	1931	
Wedenejewa	1940	
Gawel	1947	
Bappu	1952, 1953	
Leela	1953	
Beck	1958	
Tsinober & Chentsova	1959	
Chuboda	1962	
	Color centers	
Cohen	1954, 1956	impurity not specified
Frondel	1962	related to Fe substitution
Hutton	1964	Fe^{3+} substitution in tetrahedral site
Barry & Moore	1964	

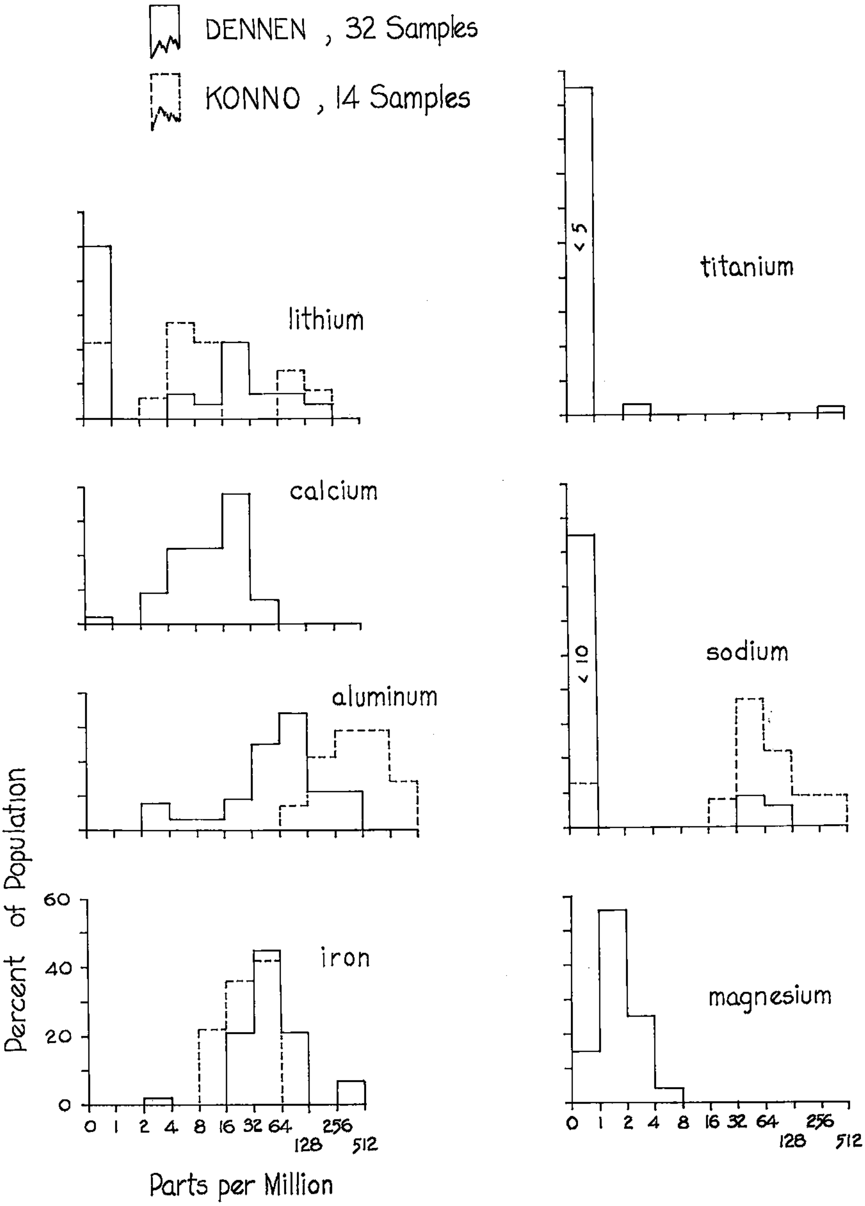

Figure 1. Distribution of contaminants in amethyst

Absorption bands in amethyst were shown by Cohen (1956) and Kats & Stevels (1956) to be produced or enhanced by *x*-irradiation and to have the attributes of color centers. Hutton (1964) and Barry & Moore (1964, 1965) have deduced by means of electron paramagnetic studies that the color center in amethyst is produced by ionizing radiation after substitution of iron in the tetrahedral site normally occupied by silicon and suggest the following mechanism :

$$\mathrm{Na^{1+}\ (Fe^{3+}O_4^{\,2-})}\ \underset{\rightleftarrows}{\mathrm{hv}}\ \mathrm{Na^{1+}\ (Fe^{3+}O_3^{\,2-}O^{1-})} + e$$

$$\text{or more simply, } \mathrm{O^{2-}}\ \underset{\rightleftarrows}{\mathrm{hv}}\ \mathrm{O^{1-}} + e$$

EXPERIMENTAL

In the present study, thirty-two specimens of amethystine quartz obtained from the U.S. National Museum and collections of the University of Kentucky were examined by emission spectrographic methods following the procedures described by Dennen (1964, 1966, 1967). Samples for analysis consisted of 5-10 mg of amethyst hand-picked under a 15X binocular. All samples were run in at least triplicate.

Analytical precision was checked by replicate determinations on single plates and by reanalysis of the same sample on different plates. The precision is not high, but variation in the concentration of non-formulary elements is much larger than the analytical error. Typically, a coefficient of variation between 10 and 20% is obtained. A comparison of results obtained by d.c. arc emission spectrography (this work) and solvent extraction-spectrophotometry for Al and Fe and flame photometry for Li and Na on similar materials by Konno (1967) is shown in Figure 1.

OBSERVATIONS AND DISCUSSION

The distribution of detectable trace elements in these samples is shown in Figure 1 together with some data from Konno (1967). The absence of Mn (<5ppm in all samples) and the nearly complete absence of Ti confirms the unimportance of these elements in the coloration of amethyst. Other elements appear to be at or near normal levels for ordinary clear quartz (Dennen 1964, 1966; Frondel 1962). However, there is a notable paucity of the alkali metals, aluminium is somewhat low, and iron is somewhat greater than average.

The non-formulary trace constituents found should substitute in quartz in stoichiometric balance with $\mathrm{Al^{3+}}$ and $\mathrm{Fe^{3+}}$ assumed to replace

Si^{4+} in a tetrahedral site and concomitant entry of other ions in interstitial positions (Dennen 1966). Some or all of the iron found in all of the samples tested must be Fe^{3+} in a tetrahedral site in order that stoichiometric balance obtain, which is consistent with EPR observations.

Since the color of amethyst results from the incorporation of Fe^{3+} in a tetrahedral site followed by irradiation, the growth conditions of amethyst must be appropriate for this substitution to occur in competition with Si^{4+} and Al^{3+}. These conditions are :

1. Growth solution composition — Fe-rich and/or Al-poor.
2. eH — oxidizing with respect to ferrous-ferric iron.
3. Pressure — low, since the ionic radius of Fe^{3+} is greater than Si^{4+} or Al^{3+}. (Sorokin 1968, has shown a significant increase in cell size with color intensity).
4. Temperature — moderate, since incorporation of the larger Fe^{3+} ion should increase with rising temperature. (The larger ionic size of iron is somewhat offset by its similarity in electronegativity to silicon compared with aluminium).
5. Post-crystallization irradiation to develop the color center.

The typical distribution of color in amethyst crystal from a colorless base to an upper portion showing amethystine zones suggests important changes in the growth environment with time and provides some insights to their geochemistry. The possible mechanisms would appear to be :

1. A change from reducing to oxidizing conditions with time.
2. A change in solution composition from Fe-poor to rich, Al-rich to poor, or low to high radioactivity with time.
3. A rise in temperature.
4. A drop in pressure.

Table 2 provides some comparative chemical data for a number of bicolored crystals. In going from a colorless base to an amethystine upper portion, the ratio Al/Fe increased in three instances, $\frac{\text{Al/Fe amethystine}}{\text{Al/Fe colorless}} = 3.3$, was unchanged in one case, and decreased in ten specimens, $\frac{\text{Al/Fe amethystine}}{\text{Al/Fe colorless}} = 0.37$ to 0.09 (median = 0.25). It appears, therefore, that in the majority of cases either the depositing solutions became more iron-rich or more oxidizing as the crystals grew. Since, however, the absolute amount of iron is seen to increase from colorless to amethystine portions, it is concluded that an increasingly iron-rich nutrient solution is primarily responsible for the color change.

Table 2. Comparative Trace Chemistry of Colorless and Amethystine Portions of the same Crystal

Sample number and location	Colorless/amethystine, ppm					
	Al	Ca	Fe	Li	Mg	Na
U.K.* Collection Thunder Bay, Ont.	160/50	52/56	8/94	20/23	1.0/0.4	82/0
U.K. Collection Unknown	46/52	4/7	28/31	5/7	4.4/0	0/0
U.K. Collection Brazil	70/50	26/11	44/280	0/19	2.3/1.2	0/0
N.M.** 47135 Hoki, Japan	17/56	11/10	26/25	46/0	9.3/1.2	0/0
N.M. 106083 Mt. Hakugan, Korea	20/34	16/14	34/35	0/0	2.0/0.8	0/0
N.M. C1179 Cape Blomiden, N.S.	10/27	3/13	10/60	0/0	1.7/3.3	0/0
N.M. C5604 Montana	110/2	25/9	23/50	0/0	1.8/0.9	0/0
N.M. 115154 Bochorice, Czech.	180/155	24/40	75/110	175/135	1.9/1.2	160/0
N.M. 92763 Dutton's Mill, Penna.	47/10	20/19	44/84	0/0	2.1/1.2	0/0
N.M. 118265 Charlotte Court Hse, Va.	64/32	4/3	38/44	22/21	1.2/1.5	0/0
N.M. 81413 Schemnitz, Czech.	50/110	—	26/110	—	0.7/1.5	—
N.M. C116B Guanajuato, Mex.	250/35	17/3	22/35	50/37	2.1/1.2	0/0
U.K. Collection Los Alamos, N.M.	125/186	—	7/27	69/73	8.7/1.4	0/0
n	13	11	13	12	13	12
amethystine enriched	6	4	12	4	3	0
colorless enriched	7	7	1	4	10	2
unchanged	0	0	0	4	0	10
% amethystine enriched	46	36	92	33	23	0
% colorless enriched	54	64	7	33	77	17
% unchanged	0	0	0	33	0	83

* U.K., University of Kentucky

** N.M., U.S. National Museum

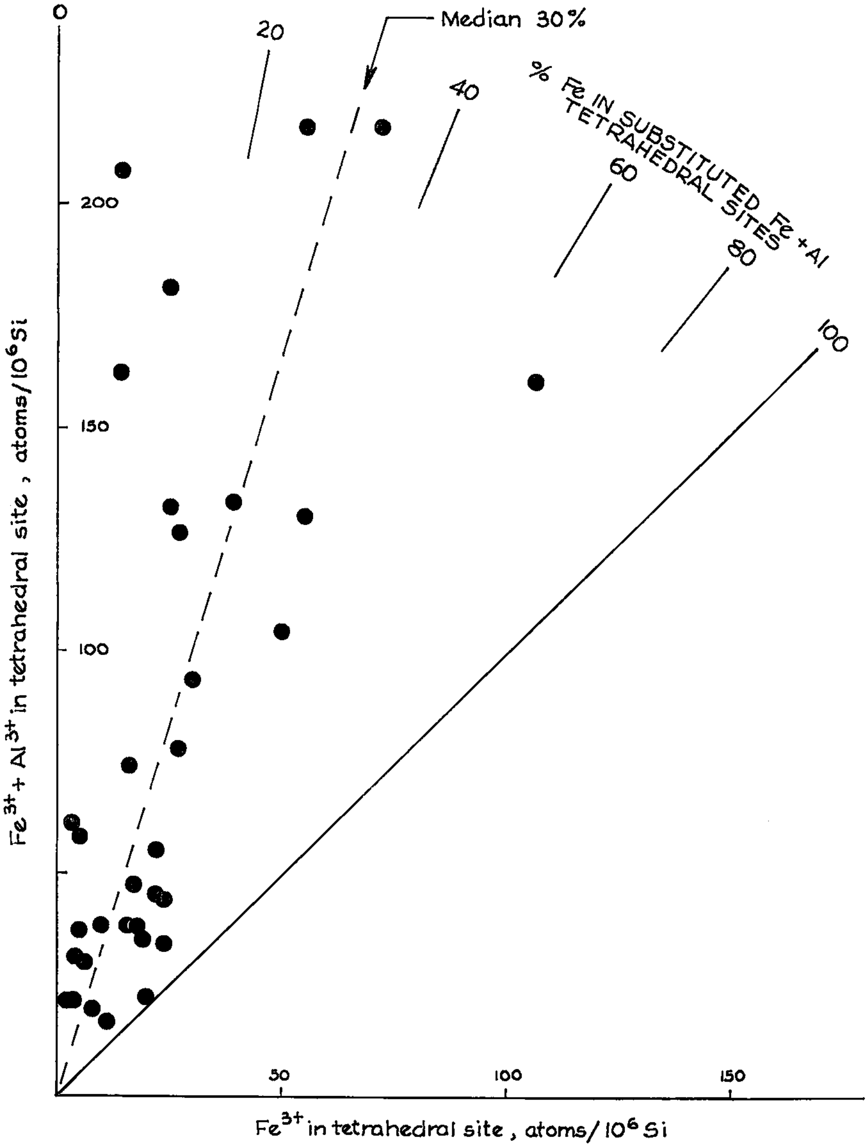

Figure 2. Iron occupancy of tetrahedral site in amethyst

The aluminum content of the clear basal portion of these bi-colored specimens may be used to estimate their temperature of crystallization (Dennen 1970). The values obtained have an excessive range (69 to 933°C), but if the higher temperature samples are presumed to be contaminated, the reasonable range of 70-285°C is obtained. This is almost exactly the range obtained by Holden (1925) of 100-250°C based on studies of inclusions.

Assuming the amethystine upper portions grew at the same temperatures and pressures as the colorless bases of the various crystals, the solubility of Fe^{3+} in the tetrahedral site as a function of temperature may be estimated from the measured growth temperatures to be 1 ppm per 5.1°C following the relation $T = 5.7x + 58$. This is approximately 0.7 of the solubility of Al^{3+} with temperature.

The location of ferric iron in tetrahedral structural sites in quartz appears to be a necessary, but not sufficient, condition for the development of amethystine color. Colorless quartz can apparently contain significant amounts of tetrahedral iron (Dennen 1966) and Table 2, and irradiation is necessary to develop a color center. The amount of iron required to trigger color activation in amethyst is not readily apparent from the data, partly due to the variable color depth of the samples examined and partly resulting from errors in analysis. Figure 2 illustrates the aluminum and iron occupancy found for the tetrahedral site in thirty-two specimens of amethyst. Very few atoms of iron in this site appear to be necessary for the development of detectable color. The proportion of iron in the total of tetrahedral proxy ions ($Fe^{3+}/Fe^{3+} + Al^{3+}$) ranges from 0.05 to 0.90 with a median of 0.30.

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