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ELECTRON MICROPROBE, X-RAY DIFFRACTION, AND SPECTRAL STUDIES OF SOUTH AFRICAN AND BRITISH COLUMBIAN "JADES"

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ABSTRACT

Electron microprobe, X-ray powder diffraction, and optical-absorption spectral studies are reported of translucent specimens of green "jade" and of pink "jade" from the Bushveld Igneous Complex. (The term "jade" is used in the sense of hard, compact, ornamental stones.) The green jade comprises inclusions of vesuvianite in a matrix of grossular, and the pink jade comprises inclusions of hydrogrossular in water-rich grossular. The optical spectra indicate that the green color is generated by Cr^{3+} and the pink by Mn^{3+}. Ninety percent of the Fe in the green stones is Fe^{3+}. Similar studies of a white jade from Lytton, British Columbia, demonstrate that the Lytton jade and the green jade are similar in chemistry and in mineralogy, confirming that the origin of color can be rationalized with crystal-field theory.

SOMMAIRE

Des échantillons translucides de "jade" vert et de "jade" rose, provenant du complexe igné du Bushveld, ont été étudiés à la microsonde électronique, par diffraction des rayons X (méthode des poudres) et par spectroscopie d'absorption optique. (Le mot jade est employé au sens de pierre ornementale, dure, compacte.) Le jade vert contient des inclusions de vésuvianite dans une gangue de glossulaire, et le jade rose, des inclusions d'hydroglossulaire dans un glossulaire riche en eau. La couleur verte est due à Cr^{3+}, et la couleur rose, à Mn^{3+}. Quatre-vingt-dix pour cent du fer, dans les pierres vertes, est ferrique. Des études analogues effectuées sur un jade blanc de Lytton (Colombie Britannique) le révèlent chimiquement et minéralogiquement semblable au jade vert, confirmant ainsi que l'origine de la couleur verte peut s'expliquer par la théorie du champ cristallin.

INTRODUCTION

The term hydrogarnet describes garnet in which the principal substitution is hydroxyl groups for SiO_4 groups. The important natural hydrogarnets are the hydrogrossulars, defined by Zabinski (1966) as OH-containing members of the series $Ca_6Al_4Si_6O_{24}$ (grossular) – $Ca_6Al_4(OH)_{24}$ with $a > 11.85$Å. Hutton (1943) described grossulars containing 4.6% H_2O^+, which is equivalent to a $Si^{4+}:4H^+$ ratio of 5:1, and applied the term hydrogrossular to them. Flint *et al.* (1941) demonstrated by hydrothermal synthesis that solid solution is complete between grossular and end-member $Ca_6Al_4(OH)_{24}$. They showed that substitution of OH into the grossular structure decreases the refractive index and increases the cell size from $a = 11.85$Å in grossular to $a = 12.56$Å in $Ca_6Al_4(OH)_{24}$. They also recognized that plazolite and hibschite, $Ca_6Al_4Si_4O_{16}(OH)_8$, are members of the grossular – $Ca_6Al_4(OH)_{24}$ series. Nuclear magnetic resonance and neutron-diffraction measurements (Cohen-Addad *et al.* 1963) of $Ca_6Al_4(OH)_{24}$ have confirmed that OH groups replace SiO_4 groups. Natural garnets of composition between hibschite and $Ca_6Al_4(OH)_{24}$ have not been reported.

The mineralogy and the chemistry of the massive garnet (grossular) deposit in the Bushveld Igneous Complex have long been of interest. These grossulars have been known as South African Jade, the term jade being used in the sense of compact, tough minerals which are suitable as ornamental stones. The grossular layers, which are interbedded with layers of anorthosite, pyroxenite, and chromite, result from the metasomatic replacement of pre-existing anorthosites and pyroxenites. Hall (1925) showed that the green and the pink jades are of similar chemical composition to grossular. The presence of OH groups was confirmed by the infrared study of van der Lingen (1928). From chemical analyses and physical properties, Tilley (1957) and Frankel (1959) concluded that the South African jades are hydrogrossular.

Zabinski (1966) reviewed the literature on hydrogarnets and examined in detail, among jades from other localities, those from South Africa, using X-ray diffraction, DTA, and infrared spectroscopy. He showed that the South African jades were inhomogeneous: the green jades comprised grossular (a=11.85 Å) and vesuvianite, and the pink comprised grossular (a=11.88Å) and hydrogrossular (a=11.96Å). Zabinski proposed the following classification for members of the grossular-hydrogrossular group:

(a) Ca-Al garnets with a=11.85Å are grossular. If the anhydrous nature is confirmed or it is to be stressed, they are anhydrous grossular.

(b) Members that contain sufficient OH to raise the value of a significantly above 11.85Å, say 11.90Å or greater, be termed hydrogrossular.

(c) Garnets containing 1% H_2O and which have a=11.85Å be termed pseudohydrogrossular. Zabinski assigned the green South African jade to this group, even though he acknowledged the presence of a sub-microscopic phase.

Such a classification is useful, with the possible exception of group (c). The role of water in low-water (say, <1% H_2O) grossular is not well-understood, particularly because it is difficult to prove that such water is structural. There is evidence, from syntheses and from spectral studies, to suggest that most grossular crystals are hydrous (Yoder 1950; Manning 1973; Manning & Tricker 1975); the proportion of grossular crystals with <0.1% structural water may be small (Wilkins & Sabine 1973; Slack & Chrenko 1971; Manning & Tricker 1977).

The two phases present in the pink and in the green jades were confirmed by McKague (1966), who also reported that the optical spectra of several jades contained a line of 4635Å (21600 cm^{-1}). This line probably represents the $^6A_1 \rightarrow {}^4A_1\ {}^4E(G)$ field-independent transition in octahedrally-bonded ferric ions in vesuvianite (Manning 1976). We have been unable to reproduce this band for specimens up to 0.1 cm thickness, but find instead that the spectra are dominated by other stronger and broader absorptions. Hall 1925) and McKague (1966) concluded, from their chemical analyses, that green jade was colored by chromium ions and pink jade by manganese ions.

Mössbauer and optical-absorption spectral studies of grossulars (Manning & Tricker 1977; Manning 1973) have shown that absorptions of octahedrally bonded ferric ions are considerably broader than ~~are~~ corresponding absorptions in, for example, andradite garnets. This broadening was attributed to the variety of crystal-fields generated around octahedrally bonded Fe^{3+} by the partial replacement of adjacent Si^{4+} ions by $4H^+$. No optical spectrum of a grossular has been reported in which the band marking the field-independent transition $^6A_1 \rightarrow {}^4A_1\, E(G)$ is sharp, i.e., has a half-width approaching the value of 500 cm^{-1} measured for andradites. A similar mechanism, the replacement of Si^{4+} by Al^{3+} and Fe^{3+} ions, accounts for the broadening of octahedral-Fe^{3+} absorption in Mössbauer and optical-absorption spectra of schorlomite garnets (Manning 1973; Burns 1972). The grossulars studied by Manning & Tricker (1977) contained 0.22 to 0.5% H_2O, and it was suggested, as had been done by Yoder (1950), that nearly all natural grossulars contain significant amounts of structural water. Technically, therefore, nearly all grossulars may be hydrous, but for convenience, a classification according to a values is probably desirable.

The structure of garnet is well-known (Abrahams & Geller 1958) and that of vesuvianite has been determined by Rucklidge *et al.* (1975) and Coda *et al.* (1970). The principal site locations for Fe^{2+} ions are the cube in garnet, and the octahedral-Al/Fe and the 5-coordinated in vesuvianite; ferric ions, and probably Cr^{3+} and Ti^{4+} ions, prefer the octahedral positions in both grossular and andradite (Manning & Tricker 1975).

EXPERIMENTAL DETAILS

Fragments of green jade from Buffelsfontein, Rustenburg, W. Transvaal, South Africa, were

TABLE 1. ELECTRON MICROPROBE ANALYSES (WT. %) OF THREE JADES AND CORRESPONDING CHEMICAL FORMULAE (D. OWENS, ANALYST).

	Green Jade		Lytton Jade		Pink Jade	
Specimen	gross[a]	vesuv[b]	gross[c]	vesuv[d]	gross(A)[e]	gross(B)[f]
a°	11.847(4)Å		11.85(1)		11.87(1)	11.95(1)
CaO	37.4	36.0	37.5	36.7	37.7	38.0
Al_2O_3	22.3	18.4	21.8	20.4	22.1	22.1
SiO_2	39.6	37.1	40.1	36.4	35.3	33.6
MgO	n.d.***	2.3	0.15	2.3	0.2	0.2
Fe_2O_3*	0.2**	1.9	0.55	0.7	0.6	0.5
MnO	0.04	n.d.	n.d.	n.d.	0.2	0.1
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
TiO_2	n.d	n.d.	n.d	n.d.	n.d.	n.d.
H_2O[g]			0.45			
Total[h]	99.5	95.7	100.1	96.5	96.1	95.0

* For convenience, Fe concentrations given as wt. % Fe_2O_3.

** Fe_2O_3 values for three different areas range from 0.00% to 0.32%.

*** n.d. = not detected (generally <0.02%)

Approximate chemical formulae (assuming analytical deficiencies due to H_2O) based on 24 oxygens for garnets and 78 oxygens for vesuvianites.

[a] $Ca_{6.0}\ (Al_{4.0}\ Fe_{0.03})\ Si_{6.0}\ O_{24}$

[b] $Ca_{18.6}\ (Mg_{1.7}\ Al_{10.4}\ Fe_{0.7})\ Si_{17.8}\ (O,\ OH)_{78}$

[c] $Ca_{6.1}\ (Al_{3.95}\ Mg_{0.02}\ Fe_{0.06})\ Si_{6.1}\ O_{24}$

[d] $Ca_{19.5}\ (Al_{12.0}\ Fe_{0.27}\ Mg_{1.67})\ Si_{18.1}\ (O,\ OH_{78})$

[e] $Ca_{6.0}\ (Al_{3.90}\ Fe_{0.07}\ Mg_{0.05}\ Mn_{0.03})\ (Si_{5.3}\ H_{2.9})\ O_{24}$

[f] $Ca_{6.0}\ (Al_{3.85}\ Fe_{0.06}\ Ti_{0.04}\ Cr_{0.01}\ Mn_{0.01}\ Mg_{0.04})\ (Si_{5.0}\ H_{3.9})\ O_{24}$

[g] Lytton value is from a whole-rock analysis; published whole-rock H_2O^+ values for green and pink jades are ~1% and ~5%, respectively.

[h] Excluding H_2O.

donated by Dr. R. I. Gait, Royal Ontario Museum, Toronto (ROM specimen number 15351). Professor R. A. Howie, King's College, London, donated a fragment of pink jade from Buffelsfontein, Rustenburg. Dr. Gait also donated chips of white jade from Lytton, British Columbia (ROM number M30122).

Optical-absorption spectra of the jades were measured by placing polished parallel-sided slabs in the sample beam of a Cary-14 spectrophotometer, and running the spectra against glass. Mössbauer spectra of powders of the green and of the Lytton jades were measured as previously described (Manning & Tricker 1975), using equipment at the Chemistry Department, University College of Wales, Aberystwyth. Pieces of green jade were hand-picked under the microscope to reduce chromite contamination. Because of low-iron values and paucity of material, spectra took several days to accumulate.

Electron microprobe analyses were performed on a Materials Analysis Company instrument operated at 25kV and using wavelength spectrometers. The analyses, listed in Table 1, are based on ten counts from each of three different areas of matrix phase and from each of three different grains of inclusions. The data were processed by the computer program of Rucklidge & Gasparrini (1969). The standards and $K\alpha$ X-ray lines used were: Durango apatite (Ca), synthetic forsterite (Fe,Mg,Si), chemically analyzed (Geological Survey of Canada) biotite (Mn,Ti), and cleavelandite (Al). The cone of excitation of the electron beam was $\sim 2\ \mu m$, which was considerably smaller than the dimensions of the grains analyzed. No visible decomposition of the specimens occurred. Apart from Fe concentrations for the grossular phase of the green jade, analyses for major elements were reproducible to $\pm 1\%$.

X-ray powder patterns were measured by Messrs. J. M. Stewart and E. J. Murray, CANMET, Ottawa, who used 57.3 and 114.6 mm Debye-Scherrer cameras. Material isolated from one phase or the other was identified on the small camera, whereas a composite sample of the pink jade was run on the larger camera; the latter showed two sets of back-reflection lines. Cell sizes for the Lytton and for the green jade grossulars were determined on the larger camera, and 18 back-reflection lines were fitted using a least-squares program (Stewart *et al.* 1972).

RESULTS AND DISCUSSION

Green jade. X-ray diffraction and microscopic examination confirmed the presence of two main phases, the X-ray method showing that the matrix material is a grossular with a=11.847(4)Å. In polished section, the second phase appears as slightly darker inclusions and sufficient material was isolated to identify the phase as vesuvianite. These results agree with the work of Zabinski (1966). The inclusions are small ($<50\ \mu m$), are well-disseminated, and comprise 5% to 10% of the volume of the sample. Microprobe analyses and the calculated chemical formulae are presented in Table 1. The grossular phase is a "normal", low-water grossular of Zabinski's type (a).

Pink jade. Microscopic examination confirmed the presence of two phases, differing slightly in reflectivity and in the degree of pitting produced by polishing. X-ray powder patterns were indicative of two garnets, one with a=11.87(1)Å and the other with a=11.95(1)Å. The latter value is indicative of a hydrogrossular, and this is confirmed by the low summation of the analyses (Table 1), assuming that H_2O is present in greater concentration than F. The smaller cell (a=11.87Å) and the low summation of the analyses for the other garnet seem to fit the criteria of Zabinski's pseudohydrogrossulars.

Lytton jade. The matrix is a Zabinski class (a) grossular, with a=11.85(1)Å, containing inclusions of vesuvianite. Electron microprobe analyses and calculated chemical formulae are consistent with these identifications (Table 1). The volume ratio of grossular:vesuvianite is ~3:1, estimated visually. The inclusions range from 2 to 50 μm, although some are as large as 350 μm. The similar mineralogy of the white Lytton and of the green jades suggests that color does not arise from scattering.

Optical-absorption spectra. The two broad absorptions in the spectrum of the green jade (Fig. 1) are reminiscent of bands marking the well-known crystal-field transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ in octahedrally bonded Cr^{3+}. The value of 10.Dq is 16750 cm^{-1}, which is similar to that measured for Cr^{3+} in uvarovite (Manning 1969a; Moore & White 1972). No trace is seen of a sharp band at 463 nm (21600 cm^{-1}) that would indicate the presence of Fe^{3+} in vesuvianite. This is to be expected from the probe analyses, because for a section 0.05 cm thick and because vesuvianite amounts to, maybe, 5% of the volume of the specimen, the calculated absorbance is <0.01, which is undetectable. A similar calculation shows that ferric ions in the grossular phase would also give rise to undetectable absorption. The higher-energy absorption band is also considerably broader than expected for field-independent transitions in ferric ions in grossular or in vesuvianite. The color of green jade, therefore, arises from the presence of Cr^{3+} ions. The required Cr^{3+} concentration, assuming an extinction coefficient for the 16750 cm^{-1} band of, say, 30 *l* $moles^{-1}$ cm^{-1}, is ~0.1% by weight. Probe analysis does not confirm this much Cr^{3+} in either of the two phases; in fact, the estimated upper limit from the probe is 0.02%. This discrepancy may be ascribed to a number of reasons: (a) the extinction coefficient is ≫ 30 *l* $mole^{-1}$ cm^{-1} (which is unlikely); (b) Cr^{3+} ions are not uniformly distributed (the samples are not uniformly green and the 463 nm Fe^{3+} band is seen by McKague, but not by us); (c) Cr^{3+} ions are located at grain boundaries, and (d) Cr^{3+} ions are present in a submicroscopic third phase. Whole-rock analyses have shown ~0.07% Cr_2O_3 in green jade (McKague 1966; Frankel 1959).

The spectrum of the pink jade reveals broad absorptions superimposed on the low-energy limb of ultraviolet-centered charge-transfer absorption. These bands, one of which is centered at ~19000 cm^{-1} (525 nm) and another at ~14500 cm^{-1} (690 nm), are reminiscent of bands in spectra of octahedrally bonded Mn^{3+} ions in pink tourmalines (Manning 1969b) and pink muscovites (Richardson 1975). Assuming an extinction coefficient of 30 *l* $moles^{-1}$ cm^{-1} for the 19000 cm^{-1} band (*cf* Mn^{3+} bands in tourmaline spectra), the calculated Mn^{3+} concentration is 0.04%, in reasonable agreement with the probe analyses (Table 1). The great breadth of the bands suggests that Mn^{3+} ions are in both grossular and hydrogrossular phases.

Mössbauer-effect spectra. The Mössbauer spectrum of the green jade comprises a broad, poorly resolved doublet that accounts for 90% of the area under the envelope. The corresponding values of isomer shift (IS), relative to Fe foil, and of quadrupole splitting (QS) are 0.37 mm^{-1} and 0.67 mms^{-1}, respectively, and are consistent with Fe^{3+} ions on octahedral positions. The half-width (HW) is relatively large (0.65 mms^{-1}) and indicates a variety of distorted octahedral environments around the ferric ions. All parameters are in reasonable agreement with those measured for octahedral-Fe^{3+} in low-water grossulars (Manning & Tricker 1977; for four specimens IS=0.36 mms^{-1}, QS=0.60 mms^{-1} and HW=0.38 to 0.59 mms^{-1}). The corresponding values for Fe^{3+} ions in vesuvianites are IS=0.35 mms^{-1}, QS=0.42 mms^{-1} and HW=0.42 mms^{-1}

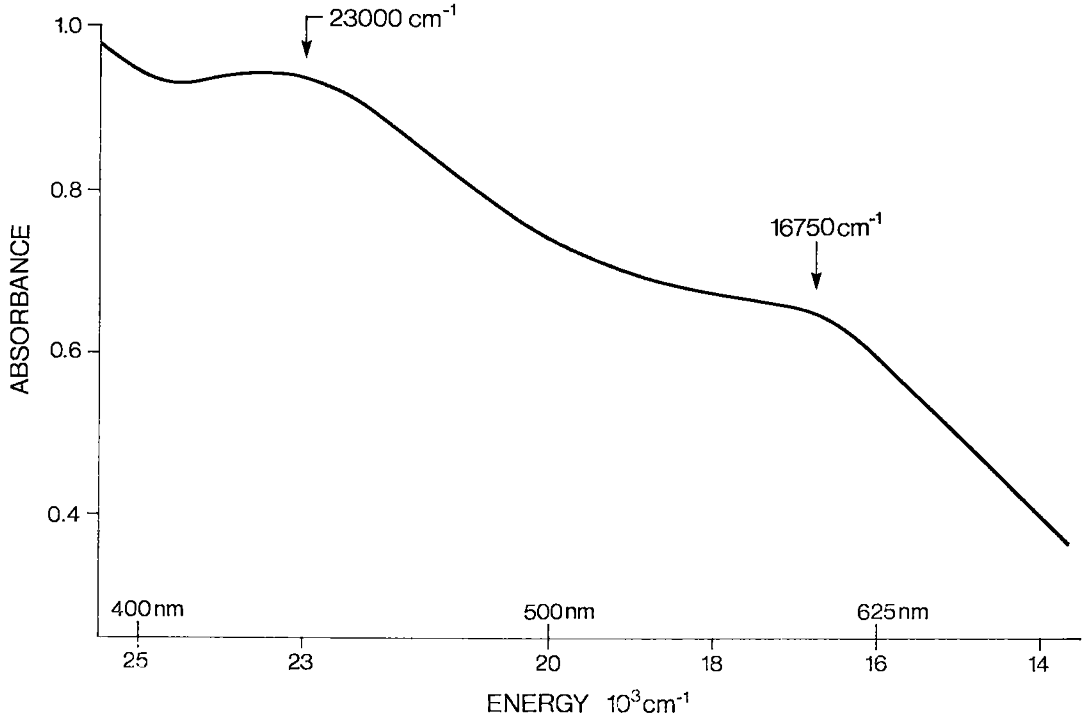

FIG. 1. Optical-absorption spectrum of green South African jade at 300K. Specimen thickness 0.05 cm. The two broad absorptions at 16750 cm^{-1} (596 nm) and 23000 cm^{-1} (435 nm) probably mark Cr^{3+} ions. The near-infrared spectrum is featureless.

(Manning & Tricker 1975). Most of the ferric ions in the whole-rock green jade specimen are therefore in grossular, further indicating, in conjunction with the chemical analyses (Table 1), that the grossular:vesuvianite ratio is $\gtrsim$10:1. Weak shoulders, amounting to some 10% of the total area under the envelope, yield values of IS=0.70 mms^{-1} and QS=3.50 mms^{-1}, and are indicative of Fe^{2+} in 8-coordination, probably in one of the four 8-coordinate sites in vesuvianite (for 8-coordinate Fe^{2+} in grossular, IS=1.26 mms^{-1} and QS=3.58 mms^{-1}; Manning & Tricker 1977).

Mössbauer spectra of the Lytton jade indicate that ferrous and ferric (IS=0.35 mms^{-1}, QS=0.57 mms^{-1}) ions are present in the ratio ~1.5:1. The spectra are not well-resolved, mainly because little material was available. The magnitude of the quadrupole splitting suggests that ferric ions are probably distributed between the octahedral positions in grossular and in vesuvianite. The ferric contents of the Lytton and of the green South African jades are similar, further suggesting that ferric ions are not the cause of color in the green jade. The Mössbauer spectrum of the pink material was not measured because of its low Fe content and insufficiency of material.

General discussion. The electron microprobe analyses of the grossular and of the vesuvianite in the Lytton and in the green jades are in good agreement. The whole-rock water content of the Lytton jade is 0.45% by weight, which is not inconsistent with the probe value assuming the deficiency in the analytical summation for vesuvianite is due mainly to H_2O. The whole-rock water content of the green South African jade has been measured to be 1.2% (Frankel 1959) and 2.3% (Zabinski 1966); the probe analyses (Table 1) are more consistent with the lower value.

The microprobe values for Mg in the green and in the Lytton jades show that Mg partitions almost wholly into the vesuvianite. The 2.3% MgO found in the vesuvianites of the two jades is consistent with MgO levels (~2%) in vesuvianites generally (Deer *et al.* 1962; Ito & Arem 1970; Manning & Tricker 1975). Too, the lower MgO concentrations in the grossulars are consistent with published values (Deer *et al.* 1962; Moore & White 1972; Manning & Tricker 1977) and therefore seem to confirm the validity of the microprobe analyses.

The microprobe analyses of the two minerals in the pink jade are similar (Table 1) except that the hydrogrossular is lower in Si and is the sole host of Cr and Ti ions. This partitioning would seem to suggest that the analysis of the grossular has not been contaminated with that of the other. The low MgO values are consistent with those for grossulars generally. Assuming that the low summation of the analysis is caused mainly by H_2O, we then have consistency with the published whole-rock analyses of 4.5% H_2O^+ (Tilley 1957) and 5.1% H_2O^+ (Zabinski 1966). Surprisingly, the two phases contain large amounts of H_2O and yet their *a* values are very different. This may reflect clustering of OH groups into domains in one garnet and a more random distribution of OH-containing "tetrahedral" sites in the other. The 11.87Å grossular seems to fit the criteria for Zabinski's group (c); the cell edge is not, statistically, significantly different from 11.85Å.

The broadening of ferric ion absorptions in the Mössbauer and optical spectra of grossular can reasonably be attributed to the replacement of SiO_4^{4-} by $[4(OH^-)]$ groups. Chemical analyses indicate that natural grossulars commonly contain 0.05 to 0.5% H_2O. Because the chemistry of H_2O in low-water grossular crystals is not understood, it seems best to classify members of the grossular – hydrogrossular series according to cell size. On this basis, they can be placed into two groups, Zabinski's (a) and (b). Future research should be directed towards elucidating the role of structural water in low-water grossular crystals. In this case, group (a), which is described by *a*=11.85Å, may be subdivided into anhydrous grossular and hydrous grossular at some defined water content. The grossular in the pink jade seems to require additional work to confirm its identity.

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