

A RAMAN INVESTIGATION OF THE AMBLYGONITE–MONTEBRASITE SERIES

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ABSTRACT

In order to obtain a more accurate method of identification of minerals of the amblygonite – montebrasite series, and particularly of gemstones cut from these minerals, we undertook an investigation by Raman spectroscopy, which is known to be a non-destructive method. Therefore, nine rough minerals and gemstones of the amblygonite–montebrasite series were analyzed by Raman spectroscopy, X-ray diffraction, infrared absorption spectroscopy, and the gemological properties (density and indices of refraction) of seven faceted gemstones were measured. Firstly, the Raman signal seems to be a good indicator of the fluorine content in the specimens, and thus useful for an accurate identification. Three peaks evolve significantly as F content increases: from 599 to 604 cm^{-1} , from 1056 to 1066 cm^{-1} and from 3379 to 3348 cm^{-1} . Also, the FWHM of the peak around 3370 cm^{-1} increases from 11 to 57 cm^{-1} as F content increases. Secondly, we found that all faceted gemstones studied herein consist of montebrasite and not amblygonite as usually claimed by gemstones traders.

Keywords: montebrasite, amblygonite, Raman spectroscopy, gemstones.

SOMMAIRE

Dans le but de disposer d'une méthode d'identification plus précise de minéraux de la série amblygonite – montebrasite, et surtout des gemmes taillées dans ces minéraux, nous avons entrepris une étude par spectroscopie Raman, réputée non destructive. Neuf échantillons bruts de la série amblygonite–montebrasite ont été analysés par spectrométrie Raman, diffraction des rayons X, et spectrométrie d'absorption infrarouge. Les propriétés gemmologiques (densité et indices de réfraction) de sept pierres taillées appartenant à cette série ont été mesurées. En premier lieu, le signal Raman semble un bon indicateur de la teneur en fluor dans

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les échantillons, et est donc utile à l'identification minéralogique. Trois pics du spectre Raman varient de façon importante, de 599 à 604 cm^{-1} , de 1056 à 1066 cm^{-1} et de 3377 à 3348 cm^{-1} . La largeur mesurée à mi-hauteur du pic à environ 3360 cm^{-1} croît également de 11 à 57 cm^{-1} lorsque la teneur en fluor augmente. En second lieu, nous observons que toutes les pierres taillées examinées par spectroscopie Raman sont de la montebrasite et non de l'amblygonite, bien que seul, ce dernier terme est utilisé par les marchands.

Mots-clés : montebrasite, amblygonite, spectrométrie Raman, gemmes.

INTRODUCTION

Faceted gemstones of the amblygonite–montebrasite isomorphous series are unusual on the gemstone market. Over the last past 35 years or so, a few Brazilian deposits are known to have supplied gem-quality material. All these stones are labeled “amblygonite”. Such a name can be ambiguous: it can refer either to the mineral species, amblygonite, LiAlPO_4F , or to a mineral belonging to the amblygonite group, *i.e.*, any specimen belonging to the amblygonite–montebrasite isomorphous series, $\text{LiAlPO}_4(\text{F},\text{OH})$.

The rapid distinction between amblygonite and montebrasite is a problem as old as the original description of the two species (Descloizeaux 1871, Pisani 1872). Several physical criteria have been found to vary as a function of the F/(F + OH) value or of the F content and, thus, have been used to estimate rapidly and indirectly the F contents of any specimen belonging to the amblygonite–montebrasite solid-solution series. Among these criteria, we can report: the optical properties and density (Winchell 1926, Winchell & Winchell 1951, Černá *et al.* 1973, Greiner & Bloss 1987); the position of selected peaks in the powder-diffraction pattern (Moss *et al.* 1969, Dubois *et al.* 1972, Černá *et al.* 1973, Kallio 1978); the crystallographic parameters of the triclinic unit-cell (Černá *et al.* 1973); the position of some absorption bands of the infrared spectra (Fransolet & Tarte 1977, Groat *et al.* 1990); the position of the ^{27}Al peak on magic-angle-spinning nuclear-

magnetic-resonance (MAS–NRM) spectra (Groat *et al.* 1990). A combination of neutron diffraction and NMR techniques has also been undertaken recently (Groat *et al.* 2003).

We examine here Raman scattering spectra of minerals of the amblygonite–montebrasite series to determine whether this technique can be used to estimate semiquantitatively the F contents in any crystal belonging to the series. Interestingly, as Raman spectroscopy is a non-destructive analytical technique currently used in gemological laboratories, this method could be useful to properly identify so-called “amblygonite” faceted gemstones as well.

ANALYTICAL METHODS

Samples

We selected nine samples belonging to the amblygonite–montebrasite solid-solution series on the basis of their chemical composition, as quoted in the literature, in order to constitute a representative collection between the F and the OH end-members. All these samples are non-gem, rough crystals preserved in the mineralogy collections of the Museum National d'Histoire Naturelle, Paris (Table 1). These samples are examined in order to calibrate the Raman spectroscopic data. In addition, we investigated seven transparent faceted gems. Their optical properties and density are described in Table 2. Six of these gemstones come from Brazil without any further detailed information. Sample 176.117a, housed in the collection of the Museum National d'Histoire Naturelle of Paris, comes from Minas do Larangerais, Minas Gerais, Brazil.

Analytical methods

Chemical composition (and thus, fluorine content) of the rough samples has been determined with an electron microprobe (CAMECA SX 50) operating at a beam accelerating potential of 15 kV and a 10 nA current. Samples were mounted in an epoxy preparation and polished to obtain as flat a surface as possible to insure precise measurements. We used as standards CaF_2 for F, apatite for P, and albite for Al and Na. The standard deviation associated with the fluorine content is about 0.1%.

X-ray powder-diffraction patterns were recorded on a Philips PW–3710 diffractometer using $\text{FeK}\alpha$ radiation

TABLE 1. SELECTED SAMPLES OF THE SERIES AMBLYGONITE [LiAlPO_4F] – MONTEBRASITE [LiAlPO_4OH]

Reference number	Geographical provenance	F	Al	P	Na	Total	Amb %
176-117b	Minas Gerais, Brazil	0.32	34.82	50.49	0.01	85.64	2.5
198-58	Newry, Maine, USA	0.36	34.70	50.31	0.09	85.46	2.8
72-150	Montebras, Creuse, France	1.70	34.51	49.87	0.03	86.11	13.2
154-299	Ankipetrata, Madagascar	2.30	34.72	49.90	0.01	86.93	17.9
reserve	Arago de Valdafleres, Caceres, Spain	3.11	34.87	49.98	0.01	87.97	24.2
76-18	Hebron, Maine, USA	4.09	34.40	50.41	0.00	88.90	31.8
154-94	Picui, Paraiba, Brazil	4.51	34.59	49.63	0.38	89.11	35.1
152-90	Erajärvi, Finland	7.46	34.87	49.62	0.61	92.56	58.1
135-246	Penig, Saxony, Germany	12.51	34.69	49.62	0.32	97.14	97.4
End-member amblygonite		12.85					100

Chemical compositions (wt.%) were determined by electron-microprobe analysis.

($\lambda = 1.9373 \text{ \AA}$). Unit-cell parameters were calculated with the least-squares refinement program LCLSQ 8.4 (Burnham 1991) on the basis of corrected d values; we used $\text{Pb}(\text{NO}_3)_2$ as an internal standard.

Infrared absorption spectra have been acquired on a NICOLET NEXUS spectrometer. Each spectrum is an accumulation of 32 scans, with a 2 cm^{-1} resolution. The samples were prepared by grinding 2 mg of mineral, which was mixed into 148 mg of KBr. This mixture was then pressed into a 13-mm pellet.

Raman scattering was measured with two instruments. For the rough samples, we used a Jobin–Yvon T64000 dispersive spectrometer, with the 488 nm excitation of an ionized argon laser, a power of 200 mW, at a resolution of 1 cm^{-1} . A spectrum is an accumulation of two acquisitions of 100 seconds each. For the faceted gems, we used a Fourier Transform Bruker RFS100 spectrometer and a Nd:YAG laser excitation at 1064 nm, a power of 300 mW, and a 4 cm^{-1} resolution; each spectrum is an accumulation of 1000 scans. In addition, the indices of refraction (RI) of the faceted gems were measured using a TOPCON refractometer, and density, with a standard pycnometer.

RESULTS

Chemical composition

The results of the determination of the fluorine content of the rough samples selected for the calibration of the Raman technique are reported in Table 1. These data confirm that the samples selected are representative of the $\text{LiAlPO}_4(\text{F},\text{OH})$ series, even if only one sample presents a F content fairly close to that of pure amblygonite (12.85 wt%). Most of the rough samples consist of montebrasite, *i.e.*, with a F content less than 6.43 wt%.

X-ray diffraction

The X-ray-diffraction technique allows us to calculate the unit-cell dimensions of the nine rough samples

(Table 3). Moreover, a careful indexing of the diffraction peaks up to $70^\circ 2\theta$ leads us to identify some impurities in a few samples. Small amounts of muscovite occur in the samples 76–18 and 198–58, whereas lacroixite, $\text{NaAlPO}_4(\text{F})$, is present in sample 154–94 and likely in 152–90. The presence of lacroixite does not affect the determination of F content in montebrasite–amblygonite, as the selected points selected for chemical analysis do not show a significant Na content (*i.e.*, more than 1.00 wt% Na_2O).

Although the powder method is destructive and, consequently, not recommended in gemology, we decided to check several analytical procedures available in the literature and using X-ray diffraction to estimate indirectly the F content in the selected samples.

The first method, refined by Černá *et al.* (1973), is based on the variation of the $d(131)$ position. We calculated the $2\theta \text{ CuK}\alpha$ for the corrected $d(131)$ value, as $\lambda \text{ FeK}\alpha$ was employed (Table 3), and estimated the F content with the regression equation published by those authors (Table 4, column 2).

Kallio (1978) calculated regression equations based on the variation of the position of the (131), (141), (122) and (012) reflections, and proposed this “four-peak” method, particularly suitable for indirect determination of F contents in montebrasite. The results obtained for

TABLE 2. LIST OF THE FACETED GEMSTONES

Reference number	Shape	Color	Weight ct	ρ	α	γ	$\gamma - \alpha$	Opt. sign
YL1	cabochon	very light yellow	1.63	3.02	1.610	1.638	0.028	B+
YL2	oval	yellow	2.21	3.01	1.612	1.641	0.029	B+
YL3	oval	colorless	0.68	3.03	1.612	1.642	0.030	B+
YL4	pear	purple grey	2.10	3.00	1.610	1.640	0.030	B+
YL5	rectangle	colorless	0.50	3.05	1.610	1.640	0.030	B+/-
YL6	baguette	light yellow	1.01	3.05	1.600	1.630	0.030	B+
176-117a	oval	yellow	32.06	3.02	1.612	1.645	0.033	B+

All the faceted gemstones studied herein come from the private collection of Yves Lulzac, except for sample 176-117a, from the Museum National d'Histoire Naturelle, Paris.

TABLE 3. CRYSTALLOGRAPHIC PARAMETERS AND 131 REFLECTION OF THE ROUGH SAMPLES

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	$d(131)$ (Å)
176-117b	5.192(1)	7.170(1)	5.041(1)	112.35(2)	97.92(2)	67.85(2)	160.74(4)	1.748
198-58	5.200(1)	7.168(2)	5.039(1)	112.30(2)	97.88(3)	67.84(2)	160.92(5)	1.752
72-150	5.187(2)	7.171(3)	5.042(2)	112.48(3)	97.96(4)	67.83(3)	160.51(7)	1.749
154-299	5.170(1)	7.173(2)	5.048(1)	113.00(2)	98.10(2)	67.66(2)	159.38(5)	1.745
Réserve	5.186(2)	7.167(2)	5.044(2)	112.64(2)	98.02(3)	67.76(3)	160.11(6)	1.747
76-18	5.177(5)	7.169(8)	5.047(6)	113.00(1)	98.20(10)	67.64(8)	159.4(2)	1.742
154-94	5.169(2)	7.177(4)	5.040(2)	112.88(4)	98.05(5)	67.68(4)	159.36(9)	1.743
152-90	5.163(4)	7.190(6)	5.045(4)	113.35(7)	98.26(8)	67.46(8)	158.8(2)	1.734
135-246	5.146(1)	7.202(1)	5.055(1)	113.88(1)	98.60(1)	67.31(1)	158.07(3)	1.727

our samples with Kallio's "four-peak" method are given in Table 4, column 3.

Černá *et al.* (1973) also published seven additional regression equations deduced from the variations of the crystallographic parameters and of the unit-cell volume. Although the correlation coefficients of these equations are not reliable in every case, notably because of a limited variation of the unit-cell parameters b and β , we calculated the arithmetic mean of the seven values obtained from these equations (Table 4, column 4).

Infrared absorption properties

Fransolet & Tarte (1977) proposed the use of infrared spectroscopy to estimate the F content in the amblygonite–montebrasite series. Two regression equations are calculated on the basis on the variations of the positions of the bending vibration band of the OH groups, located near 800 cm^{-1} , and of the stretching vibration band near 3400 cm^{-1} . The mean of the two F contents calculated in this way are listed in Table 4, column 5.

To compare the F contents measured with the electron microprobe and the F contents indirectly obtained by these methods, we calculated the regression lines and their respective correlation coefficients. Both the equations and correlation coefficients also are reported in Table 4. As these semiquantitative methods are all destructive and not really useful in the present case, our objective is not to choose the most reliable one among these methods. However, the results of the correlations presented in Table 4 tend to show that analytical measurements are reliable. The samples may thus reasonably serve as valid chemical standards with

which to calibrate the Raman characteristics of the amblygonite–montebrasite series.

Raman scattering properties

A typical Raman spectrum for montebrasite and another one for amblygonite are presented in Figure 1. These two spectra show a relatively broad peak around 3375 cm^{-1} typical for the OH stretching vibration (Fransolet & Tarte 1977). The group of peaks between 1000 and 1200 cm^{-1} can be assigned to stretching vibrations

TABLE 4. RESULTS OF THE ESTIMATION OF F CONTENT BY SEMIQUANTITATIVE METHODS

Sample	1	2	3	4	5
176-117b	0.32	3.18	1.44	1.97	0.93
198-58	0.36	1.52	0.68	1.18	0.45
72-150	1.70	2.76	2.10	1.86	1.63
154-299	2.30	4.43	5.17	4.50	2.97
Réserve	3.11	3.59	2.98	2.72	2.70
76-18	4.09	5.68	4.96	4.25	4.40
154-94	4.51	5.26	5.47	4.71	4.54
152-90	7.46	9.06	7.65	7.15	8.02
135-246	12.51	12.04	11.62	11.59	11.21
6		$y \approx 1.095x$	$y \approx 1.021x$	$y \approx 0.973x$	$y \approx 0.962x$
R ²		0.788	0.871	0.891	0.973

- wt. % F measured with the electron microprobe (this work).
- F content estimated using the position of the (131) reflection (Černá *et al.* 1973).
- F content estimated using the "four-peak" method of Kallio (1978).
- F content based on the variation of the unit-cell parameters (Černá *et al.* 1973).
- F content based on the ν_{OH} and δ_{OH} infrared absorption-peak positions (Fransolet & Tarte 1977).
- F content based on regression equation (and associated R²) to evaluate the consistency between the measured and estimated values.

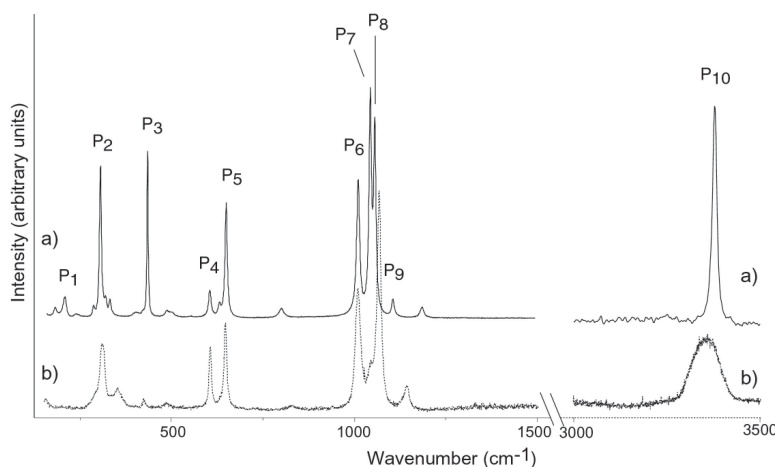


FIG. 1. Typical Raman spectra of a virtually pure montebrasite (a, sample 176.117b) and of amblygonite near the end-member composition, LiAlPO_4F (b, sample 135.246). Peak numbers refer to Table 5.

of the PO_4 anion. Below 600 cm^{-1} , the spectra are more complex, because both PO_4 bending and AlO_6 stretching vibrations mainly contribute to the absorption in this domain. One spectrum has been acquired for each rough sample previously analyzed. Positions of relatively intense peaks, as indicated on Figure 1 (P_1, P_2, P_3, \dots) have been plotted for all spectra in Table 5. Only three peaks appear to shift regularly as a function of the F contents, namely the peaks at about 600 cm^{-1} (P_4), 1060 cm^{-1} (P_8) and 3375 cm^{-1} (P_{10}). Figure 2 shows the spectra of all samples only in the vicinity of these peaks. In addition, the full width at half maximum of the peak at about 3375 cm^{-1} (called here P_{10} FWHM), is found to increase also as the F content increases. A similar variation of P_{10} and P_{10} FWHM was already observed on infrared absorption spectra by Fransolet & Tarte (1977) and by Groat *et al.* (1990), respectively. Consequently, the variations of P_4, P_8, P_{10} and P_{10} FWHM have been plotted as a function of the F contents, expressed in weight % (Fig. 3). Whereas P_4, P_8 and P_{10} seem to shift regularly with F contents, the correlation between P_{10} FWHM and the F contents is not linear.

The calculation of the regression equations and of their correlation coefficients, as reported in Table 5, clearly shows that the variations of P_4 , the Raman peak at about 600 cm^{-1} , are not sufficiently reliable. Both the slope of the curve and R^2 are decidedly weak. Although the variation of the P_8 peak is rather sensitive to the F:OH ratio, with a high R^2 , we are not able to attribute this Raman peak unambiguously. On the contrary, the

two other parameters, P_{10} and P_{10} FWHM, relating to the 3375 cm^{-1} peak, are attributable to νOH . The broadening of a peak is classically attributed to a destabilization of the molecular vibration (McMillan & Hofmeister 1988). In our case, the large amount of F replacing OH at the same crystallographic site is responsible for the lower quality of the Raman vibration at 3375 cm^{-1} in the amblygonite spectrum. The calculation of the linear regression for the variation of P_{10} as a function of F content provides an equation with both a marked slope and a rather high R^2 . However, a binomial regression equation, $y = 0.210x^2 - 5.272x + 3381.1$ with $R^2 = 0.955$, has been found to fit P_{10} variations better than the linear regression. Consequently, this last relationship appears to be the most accurate one to determine indirectly the F contents of any material belonging to the amblygonite–montebrasite series.

GEMOLOGICAL IMPLICATIONS

The gemological properties of the seven faceted gems, *i.e.*, index of refraction (RI) and density, are presented in Table 2 and Figure 4. Our measurements of RI and density give results typical of the montebrasite end-member (Descloizeaux 1871, Poirot 1976, Greiner & Bloss 1987). All faceted stones display positive biaxial properties except for sample YL5, for which the optical sign could not be determined because of similar variations of both indices. Specific gravity values range between 3.00 and 3.09, values typical for the montebra-

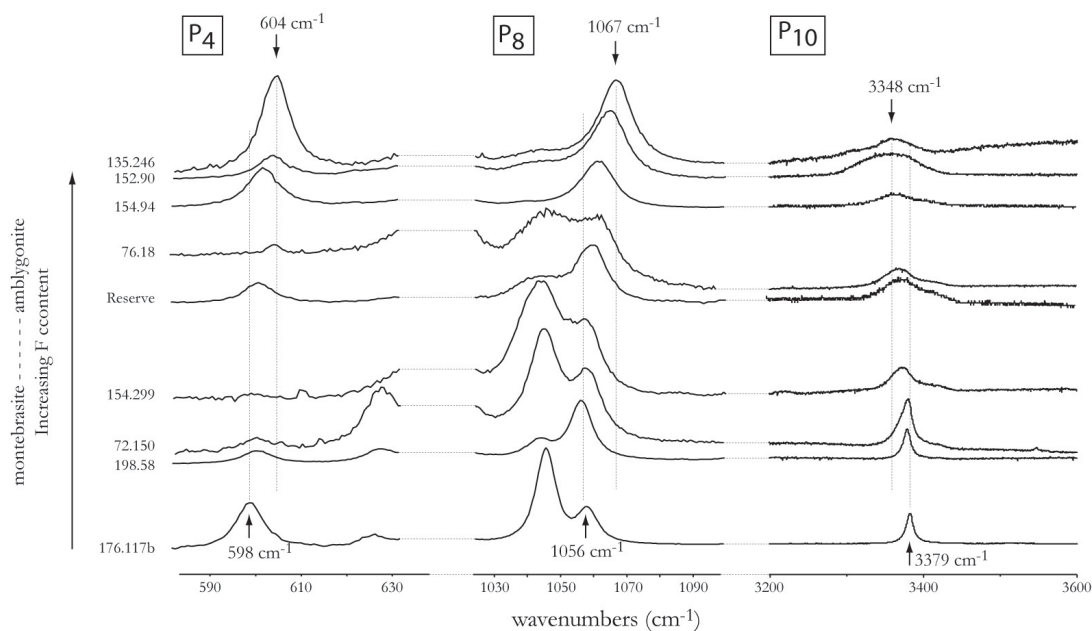


FIG. 2. Raman spectra of the rough samples. Only the peaks showing significant variations (P_4, P_8 and P_{10}) are shown for clarity.

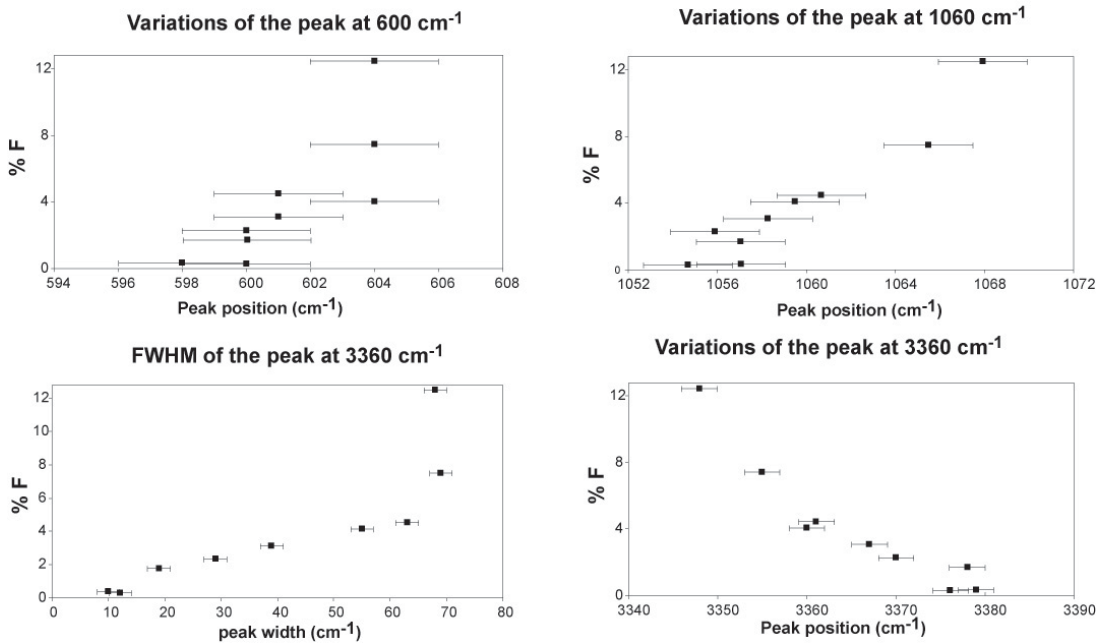


FIG. 3. Variations in position of Raman peaks and width as a function of F content. The horizontal bars indicate the standard deviation of the measurements.

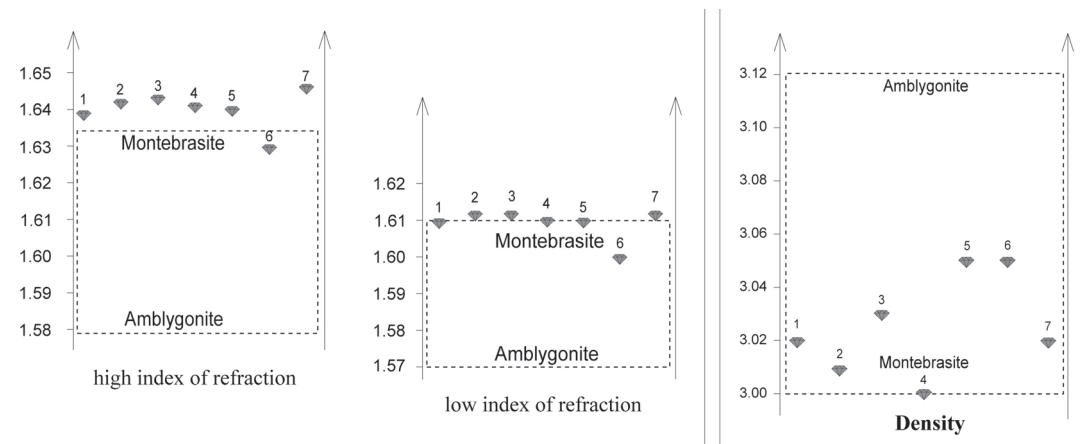


FIG. 4. Gemological properties of faceted gemstones investigated: indices of refraction and density are those of montebasite; the observed value for the highest index is higher than the previously reported values (field in gray); density and indices of refraction do not correlate well.

site end-member as well. Nevertheless, no correlation can be established between density and the two indices of refraction; for example, samples YL4 and YL5 have identical indices of refraction but contrasting densities. In taking into account the results already obtained by Winchell & Winchell (1951) and Černá *et al.* (1973),

we consider that from all these gemological properties, only the measurement of γ , the highest index of refraction, can be successfully used to estimate the F content of a sample or, in other words, its position in the $\text{LiAlPO}_4(\text{F},\text{OH})$ solid-solution series.

We acquired the Raman spectra of these seven faceted gems (Fig. 5) and measured precisely the four parameters described above (Table 6). These are used to estimate semiquantitatively the F contents of the gemstones. As the two equations with the P₁₀ variations give encouraging correlation coefficients (Table 5 and comments above), we determine indirectly from these equations the fluorine content of the seven gemstones. The results are given in the two last columns of Table 6. Surprisingly, negative values for the F contents are deduced from the linear regression equation, $y = -2.653x + 3376.7$ with $R^2 = 0.874$ (column A, Table 6). However, when the analytical uncertainties as indicated in Figure 2 are taken into account, such results are not really unrealistic. Nevertheless, the F contents calculated from the binomial equation and reported in column B, Table 6, seem to be more relevant. Indeed, the last values clearly show that most of these stones are virtually pure montebrasite, except for sample YL6, which can be considered as an example of relatively F-rich montebrasite.

Our results corroborate the ambiguity in terminology already reported in the literature by Poirot (1976). The stones are sold under the generic name “amblygonite”, which should be recognized as representing the LiAlPO₄(F,OH) series and not as the name of the mineral species. Alternatively, mineral dealers should sell these stones under the name “montebrasite”.

CONCLUSIONS

Three peaks quite visible on the Raman spectra of the amblygonite–montebrasite series (at about 600, 1060 and 3375 cm⁻¹) have been found to shift with the F content of selected rough samples of this series as standards. Moreover, the FWHM of the peak at 3375 cm⁻¹ also increases as the F content increases. These characteristics can be used to determine quickly and accurately the F content of faceted gemstones. According to this method, all of the gemstones in this study have been found to be rather pure montebrasite, in agreement with their gemological properties.

Our observations are consistent with the geological context in which minerals of the LiAlPO₄(F,OH) group are found: it is known that gem materials, such as montebrasite, usually occur in pegmatite bodies rather than in their granitic parent rocks, simply for crystal-size reasons. It has recently been shown (London *et al.* 2001) that during pegmatite crystallization, the fluorine content of the pegmatitic fluid is rapidly depleted with respect to its hydroxyl content: this is responsible for early crystallization of amblygonite in granitic intrusions, and relatively late crystallization of montebrasite. Consequently, the existence of gem amblygonite *s.s.* appears most unlikely. As all the gemstones probably come from the same field of pegmatites in Brazil, which is the only known source of gem “amblygonite” sold

nowadays, we propose the use of the term “montebrasite” for all these gemstones.

ACKNOWLEDGEMENTS

The authors are indebted to Mr. Michel Boudard, mineral dealer, for having provided all faceted stones of the Yves Lulzac private collection. The manuscript was improved thanks to the constructive comments of referees, including L.A. Groat, Associate Editor D.D. Marshall and R.F. Martin. A.M.F. is grateful for the financial support of the Fonds National de la Recherche Scientifique, Belgium, through grant 1.5.112.02.

TABLE 5. WAVENUMBERS (cm⁻¹) OF THE CHARACTERISTIC RAMAN PEAKS FOR THE ROUGH SAMPLES

	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₀ FWHM
176-117b	169	295	425	599	643	1009	1043	1056	1105	3377	11
198-58	170	297	427	600	645	1012	1045	1057	1107	3379	12
72-150	170	296	426	600	644	1011	1044	1057	1107	3378	19
154-299	n.d.	298	426	600	645	1011	1044	1057	1112	3370	31
reserve	168	299	425	601	645	1011	1044	1059	1112	3366	42
76-18	n.d.	302	426	603	646	1012	1046	1061	1111	3360	57
154-94	165	301	425	601	645	1009	1039	1061	1111	3362	55
152-90	158	304	424	604	645	1009	1043	1065	n.d.	3354	90
135-246	154	n.d.	423	604	645	1008	1043	1066	n.d.	3348	57

Regression equations and correlation coefficients also are given for the variations of P₄, P₈, and P₁₀ Raman peaks.

P₄ $y = 0.423x + 599.62; R^2 = 0.771.$

P₈ $y = 0.893x + 1056.3; R^2 = 0.898.$

P₁₀ $y = -2.653x + 3376.7; R^2 = 0.874.$

TABLE 6. CHARACTERISTICS OF RAMAN PEAKS RECORDED ON FACETED GEMSTONES AND THE INDIRECT DETERMINATION OF THEIR FLUORINE CONTENT

Reference number	P ₄ cm ⁻¹	P ₈ cm ⁻¹	P ₁₀ cm ⁻¹	P ₁₀ FWHM	A	B
YL1	600	1059	3375	12	0.64	1.2
YL2	601	1058	3378	15	-0.49	0.6
YL3	601	1057	3379	12	-0.87	0.4
YL4	600	1058	3377	15	-0.11	0.8
YL5	601	1057	3379	13	-0.87	0.4
YL6	602	1060	3367	35	3.65	3.0
176-117a	601	1057	3378	11	-0.49	0.6

The F contents deduced from the linear regression equation established with the variations in P₁₀ are given in the column A (see Table 5). In column B, the F content is calculated with the binomial equation $y = 0.210x^2 - 5.272x + 3381.1$ ($R^2 = 0.955$).

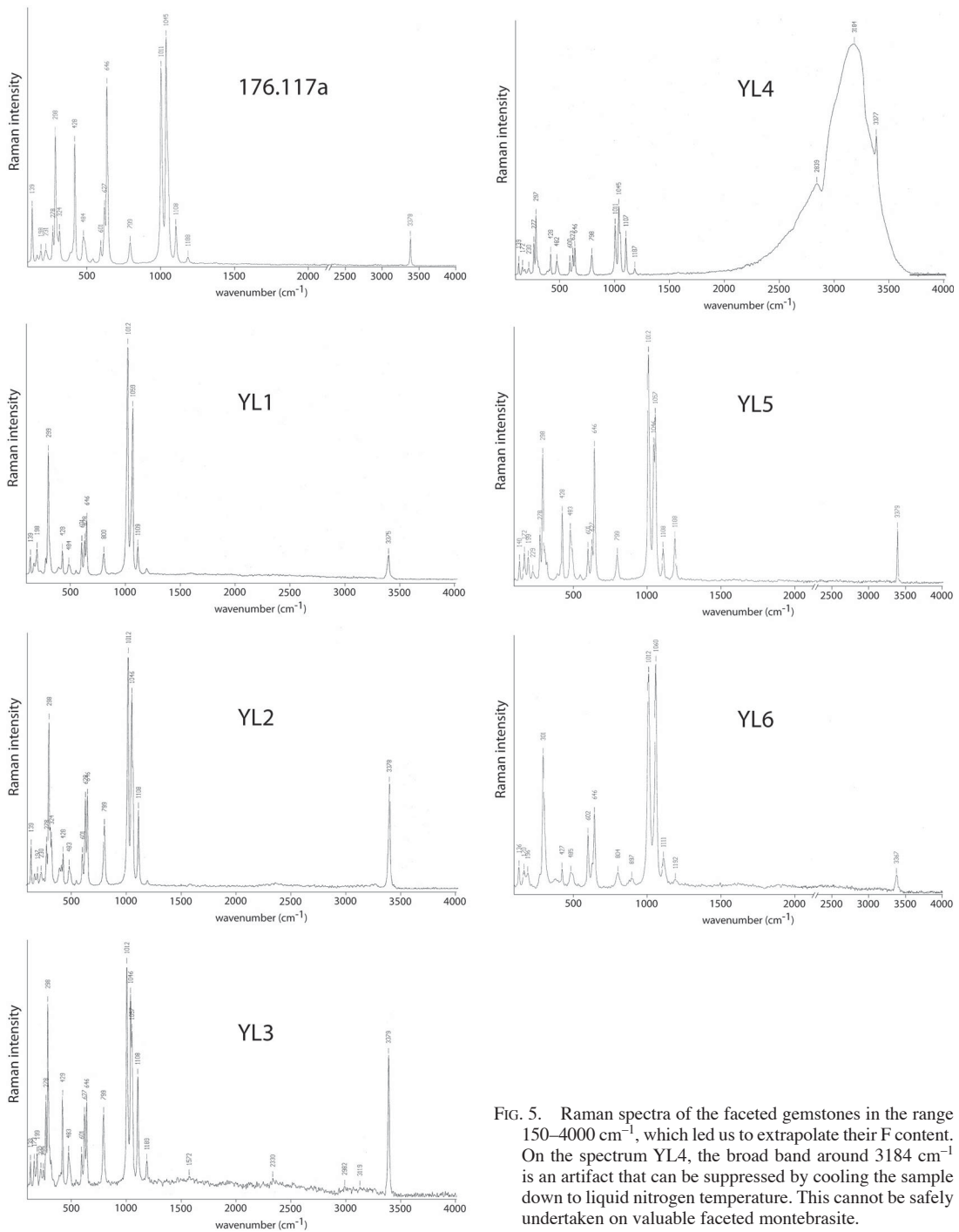


FIG. 5. Raman spectra of the faceted gemstones in the range 150–4000 cm⁻¹, which led us to extrapolate their F content. On the spectrum YL4, the broad band around 3184 cm⁻¹ is an artifact that can be suppressed by cooling the sample down to liquid nitrogen temperature. This cannot be safely undertaken on valuable faceted montebrazite.

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Received May 31, 2005, revised manuscript accepted March 24, 2006.