PEZZOTTAITE - A New Mineral

Prof. Dr. H.A. Hänni (FGA) and Dr. M.S. Krzemnicki (FGA),
SSEF Swiss Gemmological Institute, Basel, Switzerland

What at first appeared to be an extraordinary "Pink Beryl" from Madagascar has been found to be a new mineral. The text that follows was written based on the primary test results. In the course of the year 2003 research has continued and the analytical data now prove that "pink beryl" is in fact a new mineral as decided by the IMA International Mineralogical Association in September 2003. Canadian and American researchers were the first to propose a complete paper to the IMA.

In the following text the terms "pink beryl, pink morganite and Cs-beryl" should be read to mean the new mineral PEZZOTAITE.

Introduction

In mid-2002 a small quantity of pink to raspberry-red beryls was mined in Madagascar (Fig. 1). Some time earlier a minor amount of similar material had been found in Afghanistan. Pink to red varieties of beryl are reported with various names in the gemmological literature: morganite, pink beryl, and red beryl. Initial measurements made with this new material revealed surprisingly high values for refractive indices and density. These are beyond the values given in gemmological identification tables and therefore a proper explanation is required. In 2003, preliminary papers related to this new gemstone have begun to appear in gemmological journals (Gems & Gemology, Journal of Gemmology, Revue de Gemmologie a.f.g., Zeitschrift der Deutschen Gemmologischen Gesellschaft).

When its composition is close to the ideal formula, $Be_3Al_2Si_6O_{18}$, beryl is colourless and has low RI and SG values. The natural introduction of foreign elements into the structure is characteristic of many natural beryls and leads to higher values and, most importantly, when Fe, Cr, Fe, and Mn are involved, to colour. Besides these chromophore elements beryls are known to contain minor foreign elements, which are "colourless" such as Li, Sc, Cs, Rb (Deer et al., 1992). The parent rock and the growth conditions are the background, which may enable such "contaminations" and define the characteristic colour, RI and SG values.

The new material

The newly found crystals from Madagascar are from Mandrosonoro, approx. 150 km SW of Antsirabe (Central Madagascar). A pocket with crystals was found in pegmatite, together with other pegmatitic minerals such as tourmaline, kunzite, lepidolite a.s.o. Comparable material of a somewhat lighter colour was mined in Deva mine, Paroon valley

(Konar, Nuristan) in Afghanistan. Samples of both sources are crystallised in tabular hexagonal shape, and are quite semitransparent (Figures 1 and 2). The stones from Madagascar show densities between 2.91 and 3.10 g/cm^3 and RI values up to 1.608 (n_e) and 1.615 (n_o). Chemical analyses reveal very high caesium concentrations (up to 15.18 wt% Cs_2O). With such high amounts of a foreign element it becomes questionable if the mineral can still be a beryl, or if it must be considered a new mineral. Considerations of this kind have to be made by the IMA International Mineralogical Association, based on a detailed description of all data of the mineral. The data have been submitted by a large group of researchers, and we are expecting a conclusion in due course (Laurs, 2003).

Comparable beryl

In the past we have seen pink beryl, commonly called morganite, mainly from Brazil, Madagascar and Pakistan. The colour of traditional morganite is pink to almost colourless, and the colour is attributed to Mn. Morganite typically contains low concentrations of Li^+, Cs^+, and Rb^+, which make a partial so called coupled substitution for Be^{2+}. While Li replaces some of the Be, Cs and Rb compensate the charge and the ions are housed in the channel structure of the beryl crystal lattice (Bakakin et al., 1967; Hawthorne & Cerny, 1977)

Red beryl is a rare variety, from Utah, USA (Nassau & Wood, 1968; Shigley & Foord, 1984). Its colour is red to dark red, and is also attributed to manganese. The Cs content is very low; the partial substitution is very weak. Consequently the constants are low compared to beryls with higher grades of substitution.

Optical and physical data

Table 1 summarises the optical and physical data of the beryls mentioned above. Samples from Madagascar comprise a classic light pink morganite and Cs-rich "beryl" from the new source. Comparison samples are from Afghanistan and Utah, USA. Further information about the relation between chemical composition and physical values are given by Cerny & Hawthorne, 1967.

Spectroscopic characteristics

The new "pink beryls" and traditional morganites show very similar absorption spectra (Fig. 3), the new material just presenting stronger absorptions due to the higher content of Mn, and a more saturated colour. In the spectrum of the o-vibration we registered a strong maximum at 570 nm, and an absorption edge at 370 nm. The ε-vibration curve is characterised by a main absorption at 489 nm, with a side peak at 476 nm, and a second maximum at 550 nm. The absorption edge is at 370 nm, too. Remarkable is the distinct dichroism, expressed by an orange-pink and a purplish-pink vibration. The red beryls from Utah have a similar spectrum, but a definitely weaker dichroism. Spectra of Mn containing beryls were discussed by Platonov et al., 1989.

When recording the near infrared section typical water peaks were registered with morganite, pink Cs-"beryl", which is in agreement with their pegmatitic origin.

Chemical analyses

Preliminary chemical information on the new material was obtained from ED-XRF analysis. Besides the main constituents Si, Al, we noticed the presence of Fe, Mn, Cs and Rb in all samples (red beryl and pink Cs-"beryl" and

morganite). Caesium beryls have been described by Evans & Moore (1966) and Hawthorne & Cerny (1977).

Quantitative chemical analyses were performed with a JEOL-JXA 8600 electron microprobe (Geochemical Laboratory, University of Basel, Switzerland), and the results are presented in Table 1. It became evident that, compared with literature references, the Afghani sample, and even more so the samples from Madagascar, are extraordinary in their Cs content. It was expected that for each Cs^+ there would be an Li^+ located on a Be^{2+} site. Laser Ablation ICPMS analyses (Hänni & Pettke, 2003) were performed in order to investigate the presence and quantity of lithium replacing Be partially in the beryl structure. They confirm the coupled substitution mechanism (Be^{2+} -> Li^+ + Cs^+) mentioned above. Based on the quantitative analyses, the stochiometry of major and minor elements was calculated, and the formula coefficients established. It is evident that the new material from Madagascar is chemically beyond what has been reported among beryls, and we expect the material to be recognised as a new mineral.

Crystal structure data

The determination of a mineral by x-ray diffraction methods is a standard procedure, and this was undertaken with our samples, too. Some features in the diffraction pattern suggested that the new material was a beryl, but one with special characteristics. The authors decided to ask crystallographers for help. They investigated the crystal structure using x-ray single crystal methods - i.e. using the Weissenberg and Precession methods, and a Kappa CCD single crystal diffractometer. The crystal symmetry was - surprisingly - found to be trigonal (pers.comm. T. Armbruster, Bern). The crystal lattice symmetry and elementary cell dimensions were calculated from refined Bradley powder diffraction values. Quite different from normal beryls is an enlarged elementary cell, due to the considerable quantities and the highly ordered nature of the Li and Cs ions. The values of unit cell dimension are a_0 = 15.921 Å, c_0 = 27.764 Å (compared to a_0 = 9.214 Å, c_0 = 9.280 Å for beryl with the classical unit cell). Sosedko(1957) has investigated the change of structure with increasing quantities of alkalies (see table 3).

Raman spectroscopic analyses

All samples have been analysed by a Renishaw Raman microprobe (Hänni et al., 1997). Their Raman-shift spectra have been compared with references from ordinary beryls (red beryl from Utah, synthetic red beryl, and aquamarine). Figure 4 shows a partial peak shift of the pink caesium rich specimens compared to the ordinary beryls. The pink, caesium rich samples show a distinct peak at 1098cm^{-1}, whereas the reference samples have their related peak at 1069cm^{-1}. A second, but less distinct shift can be observed at 404 cm^{-1}, compared to 394 cm^{-1} for the reference samples. All other peaks show no or only minor peak shifts.

Inclusions

Based on the low number of samples we have only limited knowledge about possible inclusions in such pink Cs-"beryl" so far. The specimen from Afghanistan shows strong basal growth zoning and a few tension fractures of conchoidal shape. The samples from Madagascar contain fine tubes parallel to the c- axis (Fig. 5), and fluid inclusions flattened to the basal plane. They may be dense enough to produce cat's eye stones. (Fig. 6).

Comparison with synthetic pink, red or purple beryl

For some years hydrothermally grown red and purple beryl has been found on the gem market. The crystals appear in different colours, and owe their colour to different chromophore elements. Some of the stones have been described in gemmological literature (Henn & Milisenda 1999; Shigley & Foord, 1984). We found that none of the synthetic crystals contained Rb or Cs, but are characterised by distinct concentrations of either Ti, Mn or Ni.

The first commercially available synthetic material seems to have been pink synthetic beryl from Biron (Australia), which contains Ti as a chromophore element (Brown, 1993). Later, darker coloured synthetic crystals appeared from Russia (Fig. 7), showing distinct contents of Mn, Fe and Ni. Henn & Milisenda (1999) reported on synthetic red beryl from Russia and found Co^{2+} to be the chromophore. For all these hydrothermal synthetic beryls, the reported densities and refractive indices are clearly lower than for those of the pink Cs-"beryl" described in this study. Furthermore, we can expect most of the red to purple and pink hydrothermal synthetic material to show characteristic chevron-like growth inhomogeneities (Johnson & Koivula, 1997), not seen in natural samples.

Discussion

Caesium and lithium are typical lithophile elements involved in mineral formations in rhyolites and pegmatites. While these elements are found only in trace levels in the red beryl from Utah, in the samples from Afghanistan and Madagascar they reach minor to main element levels. Particularly in the Madagascar samples caesium reaches concentrations, which outshine any other beryls we found in literature. A consequence of these Cs concentrations is optical and physical values, which are distinctly higher than any values encountered in gemmological identification tables for beryl. Summarizing our studies of these beryls from Madagascar, they represent an extreme position in respect to all measured data (density, RI, Cs-concentration, cell parameters) compared to all beryls described so far in literature. This type of material shows so much difference in composition and physical data that it may be formulated as a new mineral, whose crystal structure is, however, closely related to beryl. The Afghani sample represents a link between the low alkali beryls and the new material from Madagascar.

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The authors can be contacted by email on: gemlab@ssef.ch

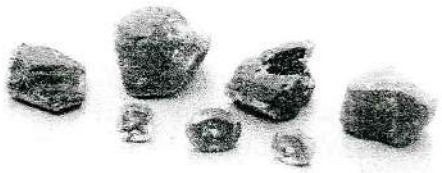

Figure 1: Pink Cs-"beryl" from Madagascar. The largest faceted stone is 3.025 ct

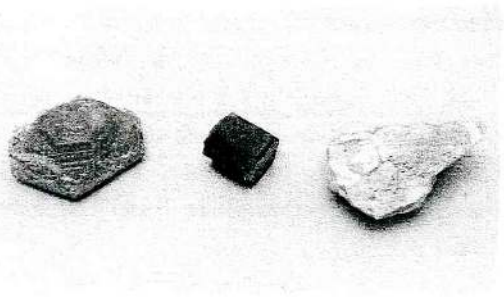

Figure 2: From left to right: pink Cs-"beryl" from Madagascar, red beryl from Utah, and morganite from Afghanistan.

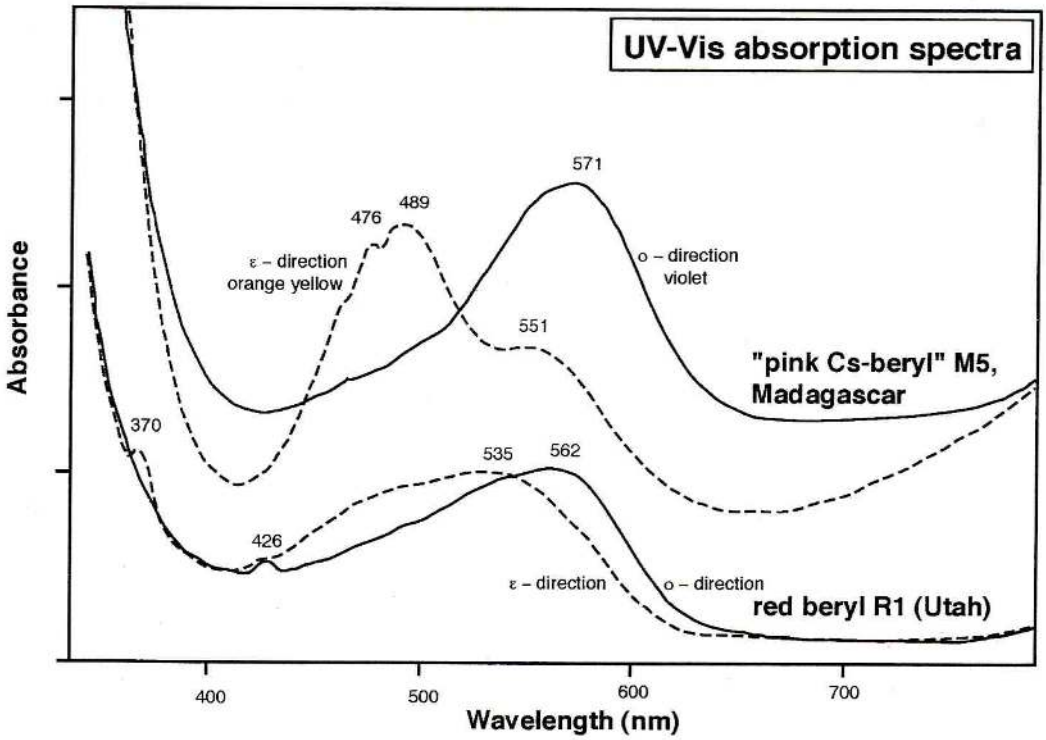

Figure 3: UV-VIS spectra of pink Cs-"beryl" from Madagascar and red beryl from Utah (USA). The spectra reveal a distinct difference between these two beryl varieties with manganese as chromophore (Mn^{2+} in morganite and Mn^{3+} in red beryl).

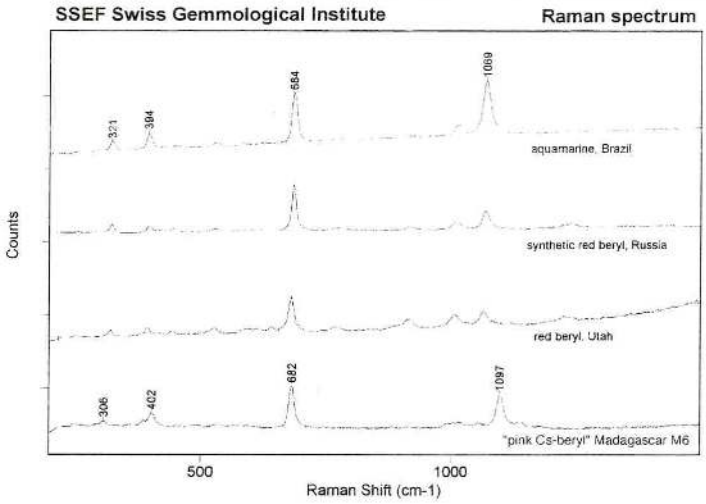

Figure 4: Raman spectra of Cs-"beryl" (Madagascar) compared with the ones of red beryl (Utah), synthetic pink beryl (Russia), and aquamarine (Brazil). Cs-rich "beryl" from Madagascar shows a distinct peak shift compared to all other beryls.

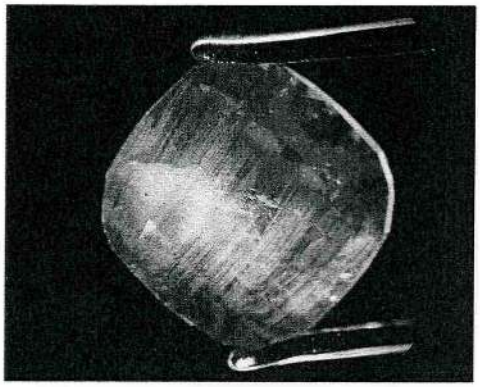

Figure 5: Cs-"beryl" from Madagascar with hollow tubes parallel to the c-axis.

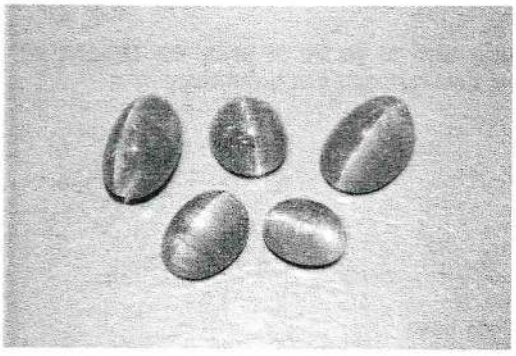

Figure 6: Cabochons of Cs-"beryl" from Madagascar showing cat's eye effect.

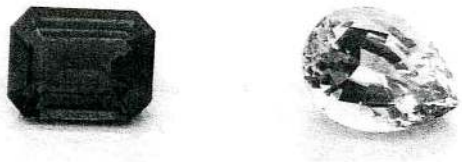

Figure 7: Hydrothermally grown synthetic beryl from Novosibirsk, Russia (left) and Biron (right).

Table 1:

Physical and optical data of "pink beryl" and red beryl

sample		density	refractive indices ne	no	DR	Cs_2O wt%
"pink beryl" (Madagascar)	M4	3.103	1.608	1.615	- 0.007	14.27
	M5	3.101	1.608	1.615	- 0.007	14.63
	M6	3.089	1.604	1.611	- 0.007	14.31
"pink beryl" (Afghanistan)	A1	2.906	1.598	1.606	- 0.008	9.70
morganite (Madagascar)	R3	2.760	1.592	1.600	- 0.008	1.09
red beryl (WahWah, Utah)	R1	2.670	1.564	1.570	- 0.006	0.13
(Thomas Range, Utah)	R2	2.670	1.568	1.575	- 0.007	

Table 2:

Chemical data of the studied specimens

	"pink beryl"				morganite	red beryl	
oxides	M4 Madagascar	M5 Madagascar	M6 Madagascar	A1 Afghanistan	R3 Madagascar	R1 Utah, USA	
BeO*	6.36	6.21	6.28	8.13	11.20	13.78	Be-site
Li2O*	1.84	1.86	1.83	1.35	0.68	0.09	
Cs2O	14.27	14.63	14.31	9.70	1.09	0.13	channel
Na2O	0.56	0.50	0.52	1.15	1.35	0.07	
K2O	0.14	0.16	0.15	0.03	0.07	0.20	
Rb2O	0.38	0.39	0.39	0.14	0.09	0.14	
MgO	b.d.	b.d.	b.d.	b.d.	b.d.	0.11	
CaO	0.17	0.17	0.19	0.98	0.01	b.d.	
Al2O3	15.84	15.70	15.62	15.72	17.52	16.59	Al-site
Cr2O3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
V2O3	0.05	0.09	0.09	0.06	b.d.	0.04	
Fe2O3	0.03	0.03	0.02	0.02	0.02	2.10	
TiO2	b.d.	b.d.	b.d.	b.d.	b.d.	0.27	
MnO	b.d.	b.d.	b.d.	0.02	b.d.	0.29	
Sc2O3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
SiO2	59.01	58.60	58.42	61.32	64.82	66.91	Si-site
total	98.65	98.33	97.82	98.60	96.85	100.692	

*BeO, Li2O, and H_2O have been calculated b.d. = below detection limit

"pink beryl" (M4, Madagscar): $(Be_{1.5}\ Li_{0.75}\ Cs_{0.65}\ Na_{0.1})_3\ (Al_{1.9},\ Fe,\ Mn)_2\ Si_6\ O_{18} * 1/2\ H_2O$

red beryl (R1, Utah): $Be_3\ (Al_{1.8}\ Fe_{0.17}\ Mn_{0.03})_2\ Si_6\ O_{18}$

Table 3:

Cell parameters

beryl variety	beryl sample	a0	c0	c/a	substitution type	oxide Cs2O	wt % Al2O3	
"pink Cs-beryl"	Madagascar M2	15.921	27.764	1.744	tetrahedral	14.4		this study
"pink Cs-beryl"	Afghanistan A1	15.951	27.829	1.745	tetrahedral	9.7		this study
morganiteRussia,	Sosendko 3	9.200	9.227	1.003	tetrahedral	4.13		Sosendko 1957
morganiteRussia,	Sosendko 2	9.202	9.209	1.001	tetrahedral	0.67		Sosendko 1957
morganiteRussia,	Sosendko 1	9.202	9.183	0.998	tetrahedral	0.27		Sosendko 1957
red beryl	Utah R1 light centre	9.214	9.206	0.999	octahedral		17.42	this study
red beryl	Utah R1 red rim	9.227	9.205	0.998	octahedral		15.74	this study
colourless beryl	Switzerland, Hänni	9.211	9.196	0.998	octahedral		18.1	Hänni 1980
aquamarine	Switzerland, Hänni	9.233	9.208	0.997	octahedral		15.5	Hänni 1980
aquamarine	Switzerland, Hänni	9.257	9.197	0.994	octahedral		14.6	Hänni 1980
aquamarine	Switzerland, Hänni	9.288	9.189	0.989	octahedral		10.6	Hänni 1980

* after Deer et al. 1992