Zircon - A Very Old Gemstone
鋯石 - 由來已久的寶石

Prof. Dr Henry A. Hänni（亨瑞 翰尼）, FGA, SSEF Research Associate

Fig. 1 A selection of zircons of various origins. The greyish cabochon is a cat's eye weighing 4.5 cts.
一組不同產地的鋯石。灰色調的素面鋯石貓眼為4.5 cts。
Photo © H.A.Hänni

本文提及兩種含鋯的常見寶石材料 — 鋯石和氧化鋯。作者詳述了鋯石的特徵 — 獨特的脫晶法，它不但影響寶石的物理特性，而且間接地形成星光或貓眼效應；同時描述鋯石的產地及顏色處理，並簡述氧化鋯的特性。

Introduction

The mineral Zircon has quite a simple chemical formula, $ZrSiO_4$; a zirconium orthosilicate. Zircons are magnificent gemstones with a high lustre, and they occur in different colours, such as white, reddish, yellow, orange and green (Fig. 1). Coloured varieties of zircon may appear in the market as hyacinth (golden to red-brown), jargon (colourless to grey and smoky), metamict (green) or starlite (blue). These terms including "matara diamond" are largely obsolete and only used in older books. Zircons from Cambodia can be heated to blue or colourless. In the early 20th century heated colourless zircons were the perfect substitute for diamonds.

Zircon crystallises in the tetragonal system, mostly as prisms with dipyramids (Fig. 2). The mineral crystallises as early formation in igneous rocks. Zircon may be over 4 billion years old. As well as hafnium and lead, Zircons usually contain traces of the radioactive elements uranium and thorium. As these decay, naturally, over millions of years, the alpha particles released gradually destroy the zircon crystal lattice, a process that is called metamictisation. The degree of metamictisation depends on the concentraton of radioactive elements and the duration of irradiation. Fig. 3 shows a qualitative ED-XRF analysis, showing the elements present in a metamict green gem from Sri Lanka.

Fig. 2 A collection of rough zircons from various deposits: On the left Mogok (Burma), on the right Tunduru (Tanzania), granite sample with zircon, Madagascar (5 cm across).
一組不同產地的鋯石晶體及原石：左：莫谷（緬甸），右：土都如（坦桑尼亞）和馬達加斯加的含鋯石的花崗岩（5厘米）。
Photo © H.A.Hänni

High zircon	**n_o1.92 – 1.94**	**n_e 1.97 – 2.01**	**DR 0.036 – 0.059**	**SG 4.65 – 4.8**
Intermediate	**n_o1.85 – 1.93**	**n_e 1.84 – 2.97**	**DR 0.008 – 0.043**	**SG 4.10 – 4.56**
Low zircon	**n 1.78 – 1.85**		**DR 0 – 0.008**	**SG 3.9 – 4.1**

(Data from Arem, 1987)

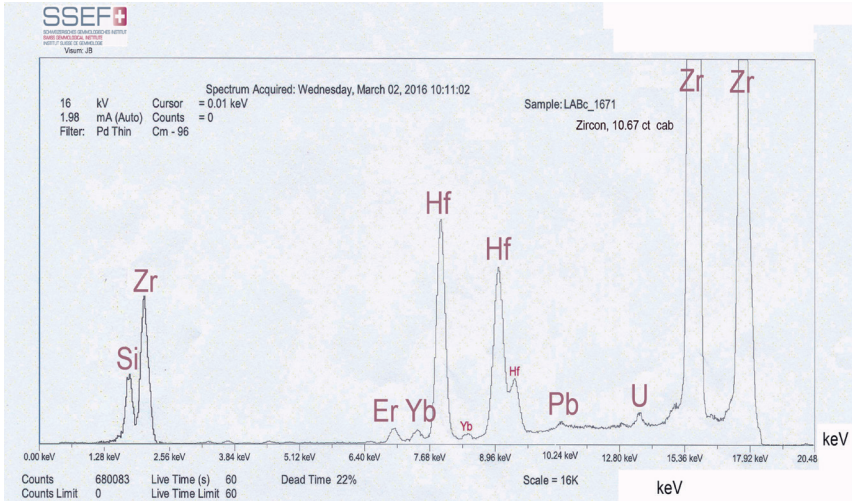

Fig. 3 Qualitative ED-XRF analysis of the metamict zircon from Tanzania in Fig. 8. Main constituents Si, Zr, REEs (Rare Earth Elements) Er, Yb, and Hf show up, as well as heavy elements U, Pb.
Spectrum by Judith Braun, SSEF Swiss Gemmological Institute
圖8的產於馬達加斯加的低型鋯石定量ED-XRF分析結果；主要成分為硅、鋯、稀土元素鉺、鐿及鉿，也包括重金屬元素鈾、鉛。
圖譜來自Judith Braun, SSEF瑞士珠寶研究院

Disorder affecting physical data

Destruction of the order in the internal lattice due to radioactive irradiation has an effect on zircon's refractive indices, birefringence and density. Fully crystallised zircons with high physical values are called High Zircons, showing strong double refraction. Zircons with a strongly damaged lattice are called Metamict or Low Zircons. These are almost isotropic. Zircons with in-between values are called Intermediate Zircons. Rough zircon is either found as perfect, prismatic crystals or as rounded pebbles in secondary deposits. Its hardness of 7½ and resistance to chemical dissolution makes it a mineral that survives metamorphism. Zircon is however a brittle mineral and is quickly worn when kept in stone papers or with other stones (Webster, 1983).

The very high birefringence of High Zircons is visible with a loupe as doubling of the back facets (Fig. 4). Hf, Th, U, and Rare Earth Elements (REEs) are heavy elements with numerous possible energy levels. Transitions between these energy levels are responsible for the many well-known absorption lines seen with the spectroscope. Inclusions in zircons may sometimes be seen as angular streaks, turbidity or fine discoid tension fractures (Gübelin & Koivula, 1986, p. 406). The latter may cause chatoyancy and, rarely, a star effect. Cathodeluminescence allows us to study growth zoning, a feature that is very common.

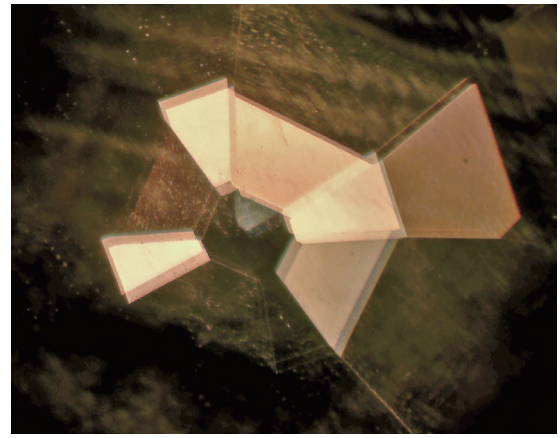

Fig. 4 A faceted octagonal step cut zircon of 24.5 cts. The back facets are visible twice. The doubling is due to the orientation of the stone (maximum double refraction perpendicular to the optical axis). Magn. 10X.
24.5 cts八角階梯切割刻面鋯石，可見亭部刻面的重影。此現象取決於寶石的觀察角度（最明顯的亭部刻面重影發生在垂直於光軸的方向）。放大倍數10X。
Photo © H.A.Hänni

Zircons as inclusions in gemstones

As zircons are among the oldest minerals and are barely affected by rock metamorphism they are found as guest minerals in many gemstone crystals. As they are crystallised in different length

to width proportions, occasionally etched or rounded, they can sometimes be used for origin determination of e.g. sapphires (Hänni, 1990). (Fig. 5)

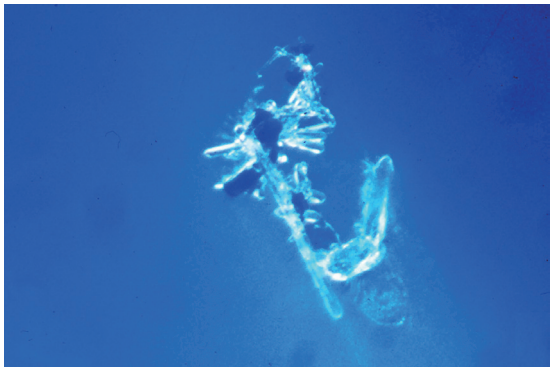

Fig. 5 A typical inclusion situation in certain sapphires from Kashmir is a cluster of long prismatic zircons, often occurring together with black cubes of uraninite. Magn. 40X.
一顆典型的克什米爾藍寶石內的長柱狀鋯石包裹體群，它經常與黑色立方氧化鈾晶體一同出現。放大倍數40X。
Photo © H.A.Hänni

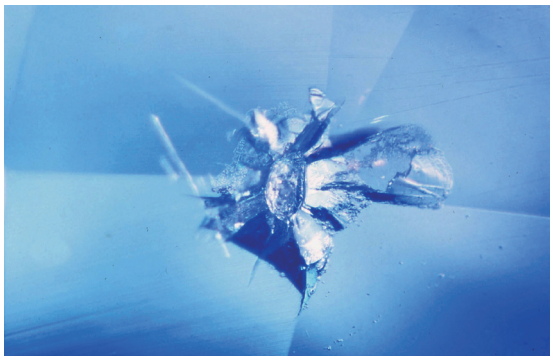

Fig. 6 A near-surface zircon inclusion in a faceted sapphire from Sri Lanka. Volume increase due to radioactive self-bombardment has increased the volume size of the crystal are causing pressure on the host sapphire. As the crystal is very near to the surface, it has blown away a part of the overlaying sapphire. Magn. 15X.
斯里蘭卡藍寶石內的一顆接近寶石表面的鋯石包裹體。其體積因鋯石自身的放射性轟擊而增大，並對藍寶石本身產生壓力。由於這顆晶體非常靠近寶石表面，它擠走了一部分表面的藍寶石。放大倍數15X。
Photo © H.A.Hänni

In unlucky cases a volume increase due to radioactive self-bombardment puts pressure on the host sapphire. If the zircon inclusion is near the surface, a sapphire chip may blow off from the overlaying portion of the host. (Fig. 6)

When zircon inclusions reach the surface of their host, age determination by the U/Pb method can be performed e.g. by LA-ICP-MS (Yuan et al., 2007). This helps to separate sapphires from different geological environments (Link, K., 2015).

As previously mentioned, zircons are often heated. Their eventually disordered crystal lattice re-arranges with the energy of the heating. A sharpening of Raman and PL peaks occurs as described in recent papers (Wang et al., 2006). By measuring Raman and PL peak proportions it is possible to estimate the temperature applied to corundum with zircon inclusions (Krzemnicki, 2010).

Stars and stripes

Chemical zonation in gem crystals is a common feature. In natural diamonds, fluorescent zoning due to preferred formation of N-aggregates can often be detected under UV light. In synthetic HPHT grown diamonds we may recognise the “Maltese cross”.

With zircons the presence of U and Th may fluctuate and reflect the availability of these elements in the period of growth. Growth bands with a higher U content expand more strongly than neighbouring bands with lower U contents. The bands with lower U contents are stretched and suffer fracturing. (Fig. 7)

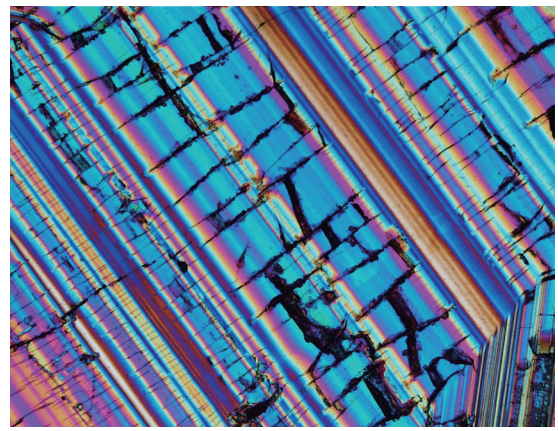

Fig. 7 Typical zonation in a zircon. The red to orange stripes are richer in U and have therefore expanded more over time. The blue bands are poorer in U and have fractured (the black lines across the bands). Thin section in polarised light, width of image 2 mm.
鋯石內部典型的帶狀結構。紅色到橘紅色的條帶顯示富集的鈾元素，並隨時間變化而變寬。藍色的條帶顯示其貧鈾，並變得有斷裂（黑線在色帶中穿插出現）。正交偏光下的礦石薄片，圖片寬度2毫米。
Photo © L. Nasdala, University of Vienna

Such fractures may develop discoid shapes and may cause different phenomena in cabochon cut stones. When the dome of the cabochon spans the discoid fractures, a sheen effect caused by reflections is seen (Fig. 8). When the fractures are cut from the side, their traces appear as fine lines, producing a cat's eye effect (Hänni & Weibel (1988), (Fig. 9). When two perpendicular systems of fractures are present (because of angular growth zoning) two cat's eye effects may cross, and we get an asteriated zircon (Krzemnicki & Steinbach, 2015). Fig. 10 shows a magnified picture of such a situation. Heat treatment applied to zircons with discoid fractures will increase the fissures, and amplify the effect.

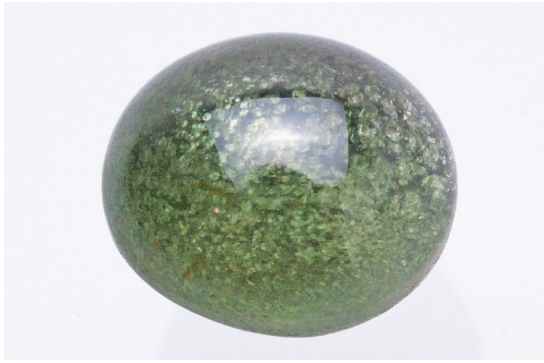

Fig. 8 A metamict zircon cabochon (10.67 cts) from Tunduru, Tanzania. Discoid fissures cause a sheen on the cabochon when they are oriented parallel to the base.
一個低型鋯石蛋形素面 (10.67 cts) 產於坦桑尼亞的土都如，其暈彩效應來自於素面寶石裏平行於底面的圓盤狀裂隙。
Photo © H.A.Hänni

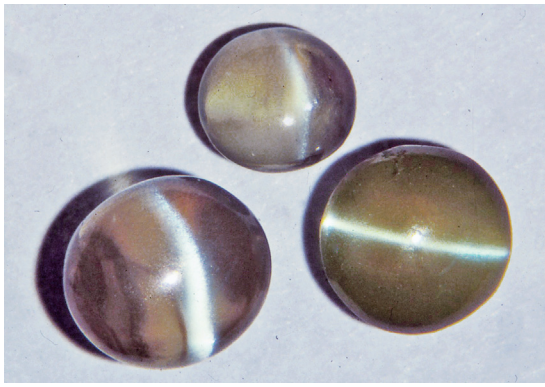

Fig. 9 Zircon cat's eyes from Sri Lanka. Tiny discoid upright fissures represent the linear elements that create the chatoyancy on the cabochons.
產自斯里蘭卡的鋯石貓眼寶石。細小的圓盤狀裂隙呈側向線性排列，使得此素面寶石產生貓眼效應。
Photo © H.A.Hänni

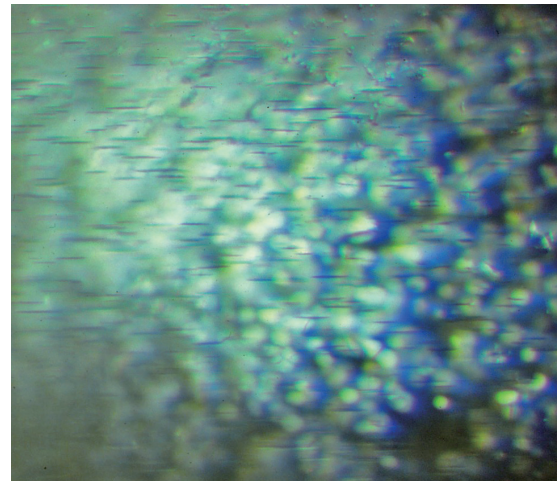

Fig. 10 Zircon cat's eye from Sri Lanka. Tiny discoid upright fissures represent the linear elements that create the chatoyancy on the cabochon. Those fissures oriented parallel to the base (dark dash-lines) cause a sheen effect. The bright ovals are discoid fissures perpendicular to the previously mentioned set. Should the cab be cut at an angle rotated 90 degrees to this orientation both systems of fissures would appear as linear elements and combine to form a two-rayed star.
產自斯里蘭卡的鋯石貓眼寶石。細小的圓盤狀裂隙呈垂直線性排列，使得此素面寶石產生貓眼效應。這些裂隙平行於底面（暗色的長橫線狀紋）產生暈彩效應。明亮的橢圓形為圓盤狀裂隙，並垂直於先前提及的裂隙組群。若此素面寶石以旋轉90度來進行拋光切割，使得其兩組裂隙分別呈線性排列的方向，則寶石會呈現有兩組星線的星光效應。
Photo © H.A.Hänni

Deposits are our sources

Zircons of cuttable sizes are found in primary rocks, as are loose crystals or rolled pebbles in placers. Major deposits are in Sri Lanka, Burma, Madagascar, Cambodia, Thailand, Tanzania, Brazil, Australia, Nigeria and Vietnam.

Colour treatments improve appearance

The thermal treatment of zircons is quite common. Nassau (1984) produced a table (shown on page 173) that describes the effects of temperature and surrounding atmosphere on different zircon materials. Intermediate zircons may restore their lattice defects at 1450°C and end up with changed colours. It is always worth trying to improve the colour of brown or reddish brown stones, which can be heated to more attractive yellow or red. The best-known heated zircons are those from Cambodia. Their original reddish brown colour becomes blue when they are heated in reducing atmosphere at 1000°C. A trade name for this blue zircon is "Starlite".

Zirconia (artificial product)

Zirconia (Zirconium-Dioxide, ZrO_2) is the name given to an artificial product. The only characteristic it has in common with the gemstone zircon is that it also contains Zr as a main chemical constituent. Zirconia crystallises in a skull melting process from a ZrO_2 melt with an amount of Ca or Y. These elements are added to stabilise the material in a cubic state (CZ stands for cubic zirconia) i.e. not doubly refractive and thus closer to the appearance of diamond. Zirconia is the stone most commonly used to imitate diamond.

Zirconia	n 2.17	SG 5.65 or 5.95 g/cm^3	Hardness 8 1/2

Manufacturers may market Zirconia under names such as Djevalite or Fianite. When doped with Rare Earth Elements and other trace elements, zirconia takes on fancy colours (Fig. 11) and may also be used as a substitute for fancy diamonds. It is, however, easy to distinguish between them with a thermotester or reflectometer.

Fig. 11 A collection of broken pieces of zirconia rough. The coloured pieces are doped with REE's. The box is 5 cm long.
一組破損的立方氧化鋯晶體。彩色的碎片含稀土元素。盒子長度為5厘米。
Photo © H.A.Hänni

Acknowledgements

Ms Judith Braun of SSEF Gem Lab took the EDS-XRF spectra of some zircons with a THERMO-Scientific, ARL QUANT'X.

Mrs Anne Carroll Marshall is acknowledged for her help with the text.

Dr Wei Zhou of SSEF Gem Lab is acknowledged for translating the captions of figures into Chinese.

References

Arem, J. E. (1987): Color Encyclopedia of Gemstones. Second Edition. Van Nostrand Reinhold, ISBN 0-442-20833-2

Deer, W.A., Howie, R.A. & Zussman, J. (1992): Introduction to the Rock-forming Minerals. Second Edition, Longman.

Gübelin, E.J. & Koivula J.I. (1986): Photoatlas of Inclusions in Gemstones. ABC Edition, Zürich, Switzerland. ISBN 3-85504-095-8

Hänni, H.A. & Weibel, M. (1988): Origin of the cat's eye-effect in heat-treated zircons from Sri Lanka. Australian Gemmologist. 16, 10, 363 - 366.

Hänni, H.A. (1990): A contribution to the distinguishing characteristics of sapphire from Kashmir. Journal of Gemmology, 22, 67-75.

Nassau, K. (1984): Gemstone Enhancement. Butterworths. P.173

Krzemnicki M.S. (2010) How to get the Blues out of the Pink: Detection of low-temperature treatment of pink sapphires. Presentation at the Seminar of The Gemmological Association of Hong Kong, March 2010.

http://www.ssef.ch/fileadmin/Documents/PDF/650_Presentations/HK2010March_PinkSapphire.pdf

Krzemnicki, M.S, & Steinbach, M.P. (2015): Zircon showing asterism. Journal of Gemmology, Gem Notes, 34, No. 8, 671 – 673

Link, K. 2015: Age determination of zircon inclusions in faceted sapphires. The Journal of Gemmology, 34(8), 2015, pp. 692-700,

Wang, Wuyi, Scarratt, K., Emmett J.I., Smith, C., Breding, M. & Douthit, T.R. (2006): Zircon inclusions in heated sapphires. Gems & Gemology, Summer, 134-150.

Webster, R. (1983): Gems, their Sources, Descriptions and Identification. 4th-Edition, Butterworths, London.

Yuan, Honglin, Shan Gao, Xiaoming Liu, Huiming Li, Detlef Günther and Fuyuan Wu (2007): Accurate U-Pb age and trace element determinations of zircon by laser ablation-inductively coupled plasma-mass spectrometry. Geostandards and Geoanalytical Research, Volume 28, Issue 3, pages 353–370.

Author's address: info@gemexpert.ch