

Gem-quality pink fluorite from Planggenstock, Switzerland: chemical and physical properties and a comparison with pink fluorites from other localities

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Introduction

In this study, first results of trace element analyses and various spectrometric investigations on pink fluorites from alpine deposits (Aar and Montblanc Massifs) as well as from the skarn deposit near Huanggang, China, will be presented.

Pink fluorite is a typical mineral from Alpine extensional fissures, especially from the granitic central massifs of the Alps Aar Massif (Switzerland) and Mont Blanc Massif (France) (Stalder *et al.*, 1998). It occurs exclusively in the form of octahedral crystals of usually less than 3 cm edge length, but very large crystals of over 15 cm are rarely found. The colour ranges from mostly pale pink to pinkish red and rarely intense raspberry red.

The formation of alpine pink fluorites occurs in connection with the formation of the minerals in alpine crystal clefts. The formation of these alpine fissures was caused by tectonic processes during the Alpine orogeny (Gnos *et al.*, 2021). At a depth of about 13 to 18 km within crustal rocks and at temperatures of 450 to 550 °C, the tectonic stress about 20 My ago led to the formation of extensional fissures in the rocks, with cavities reaching up to several metres in size. These cavities were subsequently filled with supercritical hydrothermal aqueous fluids, which dissolved minerals from the rock of the fissure walls. The cooling associated with the uplift of the Alps led to supersaturation of the dissolved complexes and thus to the hydrothermal formation of minerals in these fissures. Quartz, the most common mineral species in these Alpine clefts, started crystal formation at temperatures between about 450 and

400°C, which represents the earliest stage of crystallisation. In contrast, the crystallisation of fluorite and chlorite began at lower temperatures in the final stage of growth of the rock crystals. This is why fluorites always are found grown on the surface of quartz crystals.

Probably the largest find of alpine pink fluorite to date was made in the fissure system of the Planggenstock mountain, canton of Uri, central Switzerland. This deposit is located in the so-called Central Aar Granite, which, with an extension of about 90 km from west to east, is the largest body of granitic rock in the Aar Massif and in Switzerland. The crystal deposit was discovered in 1993 and contained several very large fissure cavities which yielded mainly rock crystal in crystals up to one metre in size. In 2019, another cavity was discovered nearby containing numerous intensely coloured and large fluorite crystals (Fig. 1 and Fig. 2) together with large amounts of green chlorite sand.

Trace elements analysis of pink fluorite

At the time of submission of this abstract, trace elements of pink fluorites from Planggenstock and Huanggang, China have been analysed using Gem-TOF (LA-ICP-TOF-MS) at SSEF. Pink fluorite samples from the Montblanc Massif (France) are currently prepared and their data integrated later.

The most abundant trace element in pink fluorites from both Planggenstock and China is yttrium, which was measured in concentrations of 170 to 278 ppm in the alpine samples and between 205 and 273 ppm in the fluorites



Figure 1: Octahedral crystals of pink fluorite on granite from the Planggenstock mountain, Switzerland.

Total height approx. 30 cm. Photo: M. Hügi

from Huanggang. Based on our samples, a clear distinction between the alpine and Chinese pink fluorites is exhibited by the varying concentrations of Sr and Lu. For both elements, the alpine samples exhibited higher mean concentrations, with factors of 3 for Sr and 8 for Lu.

Despite the divergent geochemical formation conditions, the REE patterns of both deposits demonstrate remarkable similarity in terms of concentration ranges and the ratio of light REE (LREE) to heavy REE (HREE) (Fig. 3). The REE pattern exhibited by the Chinese samples deviates from that observed in the alpine samples, and is characterised by a negative Eu - anomaly. This discrepancy can be attributed to the divergent redox conditions that prevail in the respective geochemical growth environments, as generally described by Armbruster *et al.*, (1996).

The LREE / HREE - ratio measured in the alpine fluorites also aligns with the observation by Armbruster *et al.*, (1996). These authors reported that the REE patterns of alpine fluorites and the host rock (Central Aar Granite) are contrasting, which the granite showing a notably higher LREE/HREE ratio and a slight negative Eu anomaly (Schaltegger and Krähnbühl, 1990) compared to the fluorites. The enrichment of HREE in pink fluorites can be attributed to a post-magmatic fluid-rock interaction with F-bearing fluids, which have the capacity to form complexes of HREE, in conjunction with Na, Nb, Y, Zr, Hf, Ta and U (Webb *et al.*, 1985).



Figure 2: Intensely coloured fluorite of 97.18 ct from the Planggenstock mountain, cut by Philipp Munsteiner.

Photo: Atelier Munsteiner

Cause of colour of pink fluorites

According to Bill and Calas, (1978), the attractive pink colour of fluorite is due to the presence of a YO^{2+} colour centre. This assertion is supported by UV-Vis spectrophotometry, which confirms the main absorption at 485 nm, and by the high Y concentrations that have been measured on samples both from Planggenstock and Huanggang. A weaker absorption band at 365 nm is attributed to Yb^{2+} (Armbruster *et al.*, 1996).

Some fluorite crystals from the Planggenstock show a distinct inhomogeneous colour distribution gradually ranging from intense pink to colourless. Based on our GemTOF analyses, this colour distribution is not related to variations in Y concentration. So it can be assumed that the YO^{2+} colour centres may have been activated differently due to variable exposure to natural radi-oactive irradiation.

Inclusions in alpine pink fluorite.

So far, microscopic inclusion analysis was conducted on the polished pink fluorites from the Planggenstock deposit. The inclusion pattern demonstrates the presence of two-phase fluid inclusions, which are characteristic of hydrothermal mineral formations found in the alpine fissures of the Aar massif (Mullis, 1996). These inclusions are euhedral tetrahedral negative crystals in shape and are characterised by an aqueous filling with a water vapour bubble (Fig. 4). The most prevalent solid inclusions observed on or in close proximity to the crystal faces of the fluorite crystals were layers of fine-grained chlorite, which crystallised as the final phase of mineralisation within the alpine fissure.

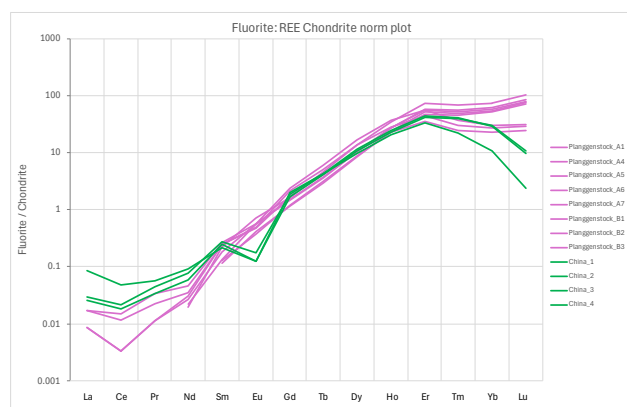


Figure 3: Chondrite-normed REE-pattern of pink fluorite of the Planggenstock mountain (red lines) resp. from the Huanggang Mine (green lines).



Figure 4: Two-phase inclusions in tetrahedral negative crystals in pink fluorite from Planggenstock mountain, Switzerland. Width of field 1.2 mm. Photo M. Hügi

Conclusions:

Although not a gemstone of great prevalence and value in the trade, fluorite, and especially attractive pink fluorite of gem-quality is considered an attractive collector stone and especially also sought after, even more so as rough crystals with or without matrix, due to their perfect octahedral shape.

With the discovery of the huge cavity with numerous pink fluorites at Planggenstock (Switzerland), and new pink flu-

orites emerging from Huanggang in China, it is the aim of this study to better characterise this new material from Planggenstock and to compare it with pink fluorites from Huanggang and the Montblanc Massif. Our preliminary results show that despite quite different geological setting and formation (Planggenstock: hydrothermal; Huanggang: skarn-related) their trace element concentrations and patterns only differ slightly.

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