

FIRST FIND OF KRISTIENSENITE IN SPAIN: COMPARISON WITH THE TYPE SPECIMEN BY NON-DESTRUCTIVE TECHNIQUES

P. Prado-Herrero¹

J. Garcia-Guinea²

E. Crespo-Feo²

V. Correcher³

C. Menor⁴

¹ MICINN, Albacete 5, Madrid 28027, Spain.(pedro.prado@micinn.es)

² Museo Nacional de Ciencias Naturales (CSIC), José Gutiérrez Abascal 2, Madrid 28006, Spain

³ CIEMAT, Av. Complutense 22, 28040 Madrid, Spain

⁴ Centro de Astrobiología (CSIC-INTA) Ctra. Torrejón-Ajalvir, Km 4 Torrejón de Ardoz, Madrid, Spain

ABSTRACT

We report herein a new find of kristiansenite from a pocket in an intra-granite pegmatite from Cadalso de los Vidrios, near Madrid, Spain. This specimen of a late hydrothermal scandium silicate has been studied by Environmental Scanning Electron Microscopy with Energy Dispersive Spectrometry probe (ESEM-EDS), Micro-Raman Spectrometry and ESEM-Cathodoluminescence (ESEM-CL), all of them non-destructive techniques. The sample is a single perfect pyramidal monocrystal found in a small cavity less than one mm across. The experimental chemical, molecular and spectral luminescent information was later compared with the type specimen from Norway and the second find, at Baveno, Italy. Our Raman spectrum matches the spectrum of the Norwegian specimen, with minor variation in the intensity of the peaks; the chemical composition recorded by EDS also shows minor variations. In addition, the CL spectrum displays several narrow peaks, probably associated with REE in Ca positions. The geochemical framework of this new locality, with pegmatite pockets in A-type granites rich in Sc-bearing minerals and other REE, have many similarities with those of Norway and Italy.

Keywords: kristiansenite, cathodoluminescence, Raman, REE

INTRODUCTION

Approved by the IMA in 2000 (#2000-51), the name *kristiansenite* honours Mr. Roy Kristiansen (born in 1943), a Norwegian mineralogist who first noticed the new mineral collected from the Hefstjærn pegmatite (of amazonite-“cleavelandite” type) 200–250 m long and 3–4 m wide, in the Tørdal area, Drangedal, Telemark County (southern Norway), the

type locality for this disilicate species. It is a triclinic *C1* (pseudomonoclinic) sorosilicate, with theoretical formula $\text{Ca}_2\text{ScSn}(\text{Si}_2\text{O}_7)(\text{Si}_2\text{O}_6\text{OH})$, described as new mineral species by Raade et al. (2002); the crystal structure was determined by Ferraris *et al.* (2001).

The second find of kristiansenite was described in the Miniera Seula (Montecatini quarry), Baveno, Verbano-Cusio-Ossola, Piemonte, Italia (Guastoni & Pezzotta,

2004). The third find, described here, is the specimen found in the granite quarries of Cadalso de los Vidrios, near Madrid, Spain. Scandium ore deposits are uncommon, and mineral species containing Sc as important constituents are scarce. Scandium is more abundant in the Earth's crust (21,9 ppm, Rudnick and Gao, 2003) than other common elements such as tin, ten times less abundant in the lithosphere. Scandium is widely dispersed in rock-forming and accessory minerals, being mainly associated with ferromagnesian minerals such as pyroxenes and amphiboles. For this reason, a small fraction of Sc is mobilized in pegmatite-related fluids; Sc is present in minerals such as helvite, milarite, epidote, and garnet. It is uncommon to find minerals in which Sc is essential constituent; in fact only nine minerals have been reported. Raade et al. (2002) explained that the incorporation of Sc in minerals is based on the similarities of the outer electronic structure of Sc, Y and some REE, in addition reflects the relatively small size of Sc^{3+} , compared with Y^{3+} and Yb^{3+} . This characteristic leads to its substitution for trivalent ions, coupled substitutions, or its incorporation in Nb and Ta minerals.

GRANITE OF CADALSO DE LOS VIDRIOS

Open working quarries produce granite blocks for ornamental purposes in Cadalso de los Vidrios, in northern Madrid, Spain. These granites were uplifted during the Hercynian Orogeny, 380–320 M.y. ago, as well as the associated metamorphic rocks (migmatite, gneiss, schist). Subsequently, they were exposed and partially eroded during the Cretaceous (120–70 M.y.) transgression, and later on, during the Alpine Orogeny

(ca. 25 M.y. ago), they rose, developing a NE–SW-trending mountain ridge known as the Spanish Sistema Central. The granites of this area are leucogranites, fine to medium grained, with an aplitic texture combined with granophyre, without phenocrysts (Pérez-Regodon, 1970). The rocks consist of orthoclase, quartz, biotite and plagioclase, as the most important mineral constituents. Pegmatite veins and cavities are rarely found in these granites, as otherwise, they would not be used for ornamental uses. They are centimetric veins, in some cases exhibiting elongate cavities with associations of unusual minerals, such as kristiansenite. The periodic inspection of the quarries of Cadalso de los Vidrios, which cover around 7 km², has yielded several samples from these pegmatites and cavities, with a wide parageneses of minerals: quartz (hyaline, smoky and amethyst), opal (hyalite), microcline and orthoclase, albite (including the cleavelandite habit), muscovite, biotite, chlorite, topaz, tourmaline (black and blue), garnet (spessartine), helvite, zoisite–clinozoisite, bavenite, beryl, fluorite, sphalerite, pyrite, pyrrhotite, arsenopyrite, bismuthinite, chalcopyrite, molybdenite, ferberite, hematite, apatite, fayalite, pyrolusite, scheelite, axinite, titanite, laumontite, prehnite, stilbite, apophyllite, laumontite, chabazite, milarite, aurichalcite, malachite, uranotile, metatorbernite, torbernite, calcite, aragonite, pyrolusite, gadolinite-(Y), allanite-(Ce), kamphaugite-(Y), britholite-(Ce), and kristiansenite, the focus of this article.

EXPERIMENTAL PROCEDURE

The kristiansenite specimen was firstly analyzed in the Inspect-S ESEM of the FEI Company of the Museo

Nacional Ciencias Naturales in Madrid. The chemical analyses were performed with an EDS probe at 30 kV and focal distance 10,4 mm on a large sample, *ca.* 5×5 cm² without coating. CL spectra and monochromatic CL images were performed in the ESEM with a direct optical coupling to a chamber-mounted Gatan MonoCL3 monochromator. The excitation for CL measurements was provided by a 30 kV electron beam. The emission current ranges between 52 and 68 mA, and the photomultiplier voltage of the PA3 amplifier was 1000 volts for the luminescence spectrum. The CL emission of kristiansenite was analyzed in low-vacuum mode without coating. The micro-Raman spectra were acquired with a ThermoScientific DRX Raman microscope, which has a point-and-shoot Raman capability of one micrometer spatial resolution. We used a green 532

nm laser with a 100% power of 10 mW, exposition time to laser 60 s, and two acquisitions each. The used objective was 50 $\times$.

RESULTS AND DISCUSSION

The specimen found in a cavity in the Cadalso de los Vidrios pegmatite is a well-formed crystal, *ca.* 0.5 mm across, with a vitreous luster; it is translucent, white to slightly yellowish, with the wedge-shaped habit typical for this species and oblique faces. It is a single crystal located in a sample of 5×5 square centimeters, with paragenetic quartz, microcline, chlorite, kamphaugite, pyrite and other unknown species containing significant amounts of Sc, Y and REE. The physical position of the crystal into the cavity (Fig. 1) makes difficult the non-destructive analytical measurements.

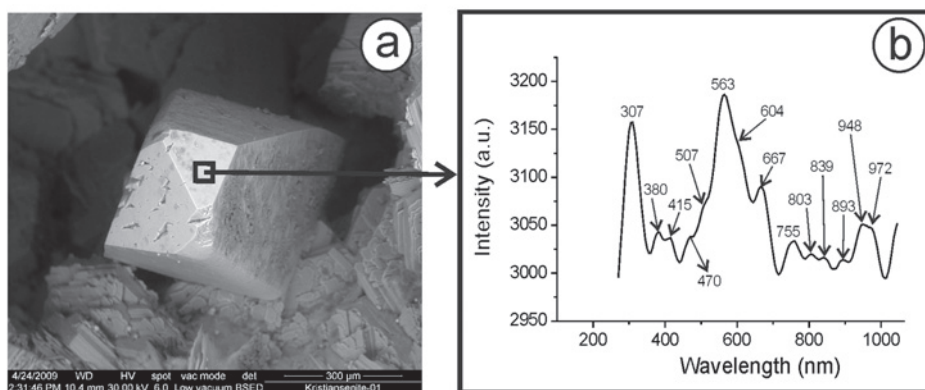


Figure 1. ESEM-CL of the kristiansenite specimen: (a) ESEM image of cavity in which is located the crystal with surrounding chlorite, (b) CL spectrum taken from the top face of the crystal.

Table 1. Comparison of the EDS analyses of holotype kristiansenite with the Spanish sample.

Oxides	Raade G. et al. (2002) (Mean of 11 analyses)	Raade G. et al. (2004). (Mean of 5 analyses)	Cadalso de los Vidrios (Madrid)
Na ₂ O	0,41		0,66
K ₂ O	0,06		
CaO	18,45	19,22	17,31
Al ₂ O ₃	0,35	0,13	2,7
Sc ₂ O ₃	8,11	11,74	3,2
Fe ₂ O ₃	1,98	0,5	4,57
SiO ₂	40,76	40,05	45,36
TiO ₂	0,08	0,18	0,93
ZrO ₂	0,43	0,28	
SnO ₂	27,33	25,42	24,09
MnO ₂		0,02	0,64
Yb ₂ O ₃			0,54
Y ₂ O ₃		0,01	
Nb ₂ O ₅		0,29	
H ₂ O	2,04	2	
Total	100	99,84	100

Table 1 displays the comparison between our EDS results with the published data of the Norwegian type-locality. One can see that: (i) the SiO₂ content is 5% higher in the Spanish case, probably due to the surrounding silicates, (ii) the SnO₂ values are very similar in all samples, and (iii) the amount of Sc₂O₃ is significantly lower in the Spanish specimen. The probable replacement of Sc³⁺ by Al³⁺ or Fe³⁺ ions in our specimen could explain the reported differences with respect to the data of Raade *et al.* (2002). The analyses performed on the associated kamphaugite display an abundance of REE, which could also explain the observed chemical variations as well as the differences between the recorded Raman spectra with respect to the Norwegian material (Fig. 2). The peaks obvious match, but minor variations in intensities and shoulders are observed.

In short, Cadalso de los Vidrios is the third geological area in which kristiansenite is found, after the type locality (Heftetjern pegmatite) and the pegmatite field at the Montecatini quarry. The three cases are similar from the point of view of the mineral parageneses, Sc-bearing minerals and other REE. The kristiansenite specimen of Cadalso de los Vidrios, as well as other Sc-bearing minerals present in this pegmatite field, commonly include REE in the parageneses and were formed during the late hydrothermal stages of

the miarolitic pegmatite formation. The mineral parageneses found here exhibits coincidences with the Tørdal case.

REFERENCES

- Ferraris, G., Gula, A., Ivaldi, G., Nespolo, M., Raade, G. 2001. Crystal structure of kristiansenite: a case of class IIB twinning by metric merohedry, *Zeitschrift für Kristallographie*, 216, 442-448
- Raade, G., Ferraris G., Gula, A., Ivaldi, G., Bernhard, F. 2002. Kristiansenite, a

- new calcium-scandium-tin sorosilicate from granite pegmatite in Tørdal, Telemark, Norway, *Mineralogy and Petrology*, 75, 89-99
- Pezzotta, F., 2004. Kristiansenite a Baveno, secondo ritrovamento mondiale della specie. *Riv. Mineral. Ital.*, 28, 4: 247-251
- Raade, G., Bernhard, F. and Ottolini, L., 2004. Replacement textures involving four scandium silicate minerals in the Heftejern granite pegmatite, Norway. *Eur. J. Mineral.* 16, 945-950.
- Garcia, G., Gonzalez, C., Bueno, A. 2004. Cadalso de los Vidrios (Madrid). *Bocamina* nº 14, 12-46.
- Menor C, Prado-Herrero, P., 2008. Kristiansenita, Britolita-(Ce) y otros minerales raros en el granito de Cadalso de los Vidrios, Madrid. *Revista de Minerales* 2008/2.