

## Crystal chemistry and hydrogen bonding of rustumite $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)(\text{OH})_2\text{Cl}_2$ with variable OH, Cl, F

FRANK GFELLER,<sup>1,\*</sup> THOMAS ARMBRUSTER,<sup>1</sup> EVGENY V. GALUSKIN,<sup>2</sup> IRINA O. GALUSKINA,<sup>2</sup> BILJANA LAZIC,<sup>1</sup> VALENTINA B. SAVELYEVA,<sup>3</sup> ALEKSANDR E. ZADOV,<sup>4</sup> PIOTR DZIERŻANOWSKI,<sup>5</sup> AND VIKTOR M. GAZEEV<sup>6</sup>

<sup>1</sup>Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

<sup>2</sup>Department of Geochemistry, Mineralogy, and Petrography, Faculty of Earth Sciences, University of Silesia, Bedzińska 60, 41-200 Sosnowiec, Poland

<sup>3</sup>Institute of the Earth's Crust SB RAS, Lermontov st. 128, 664033 Irkutsk, Russia

<sup>4</sup>Science Research Centre “NEOCHEM”, Altuf’evskoye Highway 43, Moscow, Russia

<sup>5</sup>Institute of Geochemistry, Mineralogy and Petrology, Warsaw University, al. Zwirki i Wigury 93, 02-089 Warszawa, Poland

<sup>6</sup>Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) RAS, Staromonetny 35, Moscow, Russia

### ABSTRACT

Three samples of the skarn mineral rustumite  $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)(\text{OH})_2\text{Cl}_2$ , space group  $C2/c$ ,  $a \approx 7.6$ ,  $b \approx 18.5$ ,  $c \approx 15.5$  Å,  $\beta \approx 104^\circ$ , with variable OH, Cl, F content were investigated by electron microprobe, single-crystal X-ray structure refinements, and Raman spectroscopy. “Rust1\_LCl” is a low chlorine rustumite  $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)(\text{OH}_{1.88}\text{F}_{0.12})(\text{Cl}_{1.28}\text{OH}_{0.72})$  from skarns associated with the Rize batholith near İkizdere, Turkey. “Rust2\_F” is a F-bearing rustumite  $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)(\text{OH}_{1.13}\text{F}_{0.87})(\text{Cl}_{1.96}\text{OH}_{0.04})$  from xenoliths in ignimbrites of the Upper Chegem Caldera, Northern Caucasus, Russia. “Rust3\_LCl\_F” represents a low-Cl, F-bearing rustumite  $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2[(\text{SiO}_4)_{0.87}(\text{H}_4\text{O})_{0.13}](\text{OH}_{1.01}\text{F}_{0.99})(\text{Cl}_{1.00}\text{OH}_{1.00})$  from altered merwinite skarns of the Birkhin massif, Baikal Lake area, Eastern Siberia, Russia. Rustumite from Birkhin massif is characterized by a significant hydrogarnet-like or fluorine substitution at the apices of the orthosilicate group, leading to specific atomic displacements. The crystal structures including hydrogen positions have been refined from single-crystal X-ray data to  $R1 = 0.0205$  (Rust1\_LCl),  $R1 = 0.0295$  (Rust2\_F), and  $R1 = 0.0243$  (Rust3\_LCl\_F), respectively. Depletion in Cl and replacement by OH is associated with smaller unit-cell dimensions. The substitution of OH by F leads to shorter hydrogen bonds O-H···F instead of O-H···OH. Raman spectra for all samples have been measured and confirm slight strengthening of the hydrogen bonds with uptake of F.

This study discusses the complex crystal chemistry of the skarn mineral rustumite and may provide a wider understanding of the chemical reactions related to contact metamorphism of limestones.

**Keywords:** Rustumite, crystal chemistry, skarn mineralogy, crystal structure, OH-, F-, Cl- substitution, Raman spectroscopy, hydrogen bonds