MATERIALS AND METHODS

For this study natural paracelsian originate from the Benallt Mine, Gwynedd, Wales, UK, obtained from a private systematic collection of Anatoly V. Kasatkin (Fesman Mineralogical Museum of RAS, Moscow,) was used. The chemical composition of this sample is quite simple ($Ba_{1.01}K_{0.02}Al_{1.95}Si_{2.03}O_8$). Detailed chemical analysis data were published in [Gorelova et al., 2021].

Thermal behavior of paracelsian on heating in air was studied by the high-temperature powder X-ray diffraction (HTPXRD) using a Rigaku Ultima IV diffractometer (CuKα radiation, 40 kV / 30 mA, Bragg-Brentano geometry, PSD D-Tex Ultra) with a thermo-attachment in the range 30–1110 °C with the temperature step of 30 °C. Fine-powdered samples were prepared on a platinum sample holder (20×12×1.5 mm) from an ethanol suspension [Filatov, 1971]. The external Si standard was used before the measurement to control the 2θ correctness. Calculations of the unit-cell parameters were performed using the program package Topas 4.2. [Bruker AXS 2009].

The visualization and calculation of the thermal-expansion parameters tensor were performed using the TTT program package [Bubnova et al., 2013]. The temperature dependencies of the unit-cell parameters were described by quadratic polynomial functions. The thermal expansion coefficients (TECs) were calculated using linear (for comparison with previously studied of feldspar-related minerals and compounds with paracelsian topology) and second-order polynomials.

RESULTS

Two-dimensional plot of the evolution of XRD pattern upon heating (Fig. S1) demonstrates the beginning of the transformation process of paracelsian with a formation ~7 % of celsian (polymorphic modification of $BaAl_2Si_2O_8$ with lower symmetry) at the temperature above 930 ºC. With the further temperature increasing, the amount of celsian increases and at 1110 ºC there is no paracelsian peaks on the XRD pattern. The phase composition of the sample preserves upon cooling, i.e. the paracelsian → celsian polymorphic transition is irreversible, that is in agreement with previously published data [Lin, Foster, 1968].

The temperature dependencies for the unit cell parameters, obtained during our HTPXRD experiment are shown in Fig. S2. Up to 930 °C the crystal structure of paracelsian undergoes a continuous expansion of all unit cell parameters, except β angle, which slightly decreases with the temperature increasing. At higher temperatures the behavior of the unit cell parameters is not

so continuous due to the transformation process. As a consequence, though, the unit-cell parameters were calculated in the whole studied temperature range, the TECs were calculated only up to 900 ºC (Table 1).

The thermal expansion of paracelsian has very anisotropic character (Fig. S2, S3; Table 1): $\alpha_{max}/\alpha_{min}$ = 12. The anisotropy of paracelsian increases with the temperature increasing up to the negative TEC along the one direction (α_{22}) (Fig. S3). Directions of the maximal and minimal thermal expansion is close to the *a* and *b* axes, respectively. In other words, the maximal thermal expansion of paracelsian is along crankshaft chains.

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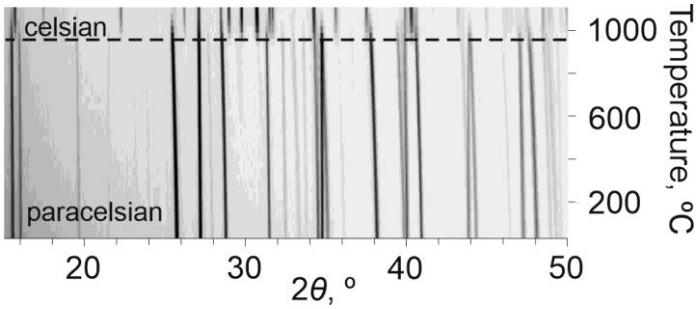

Fig. S1. The 2D-plot of the powder XRD data of paracelsian → celsian transformations in the temperature range 30–1110 ºC. The broken line shows the start of the transformation process of paracelsian to celsian.

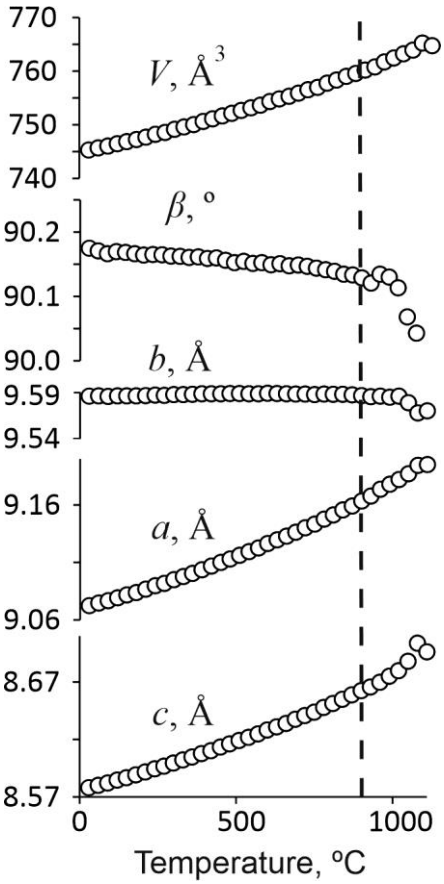

Fig. S2. The unit-cell parameters of paracelsian at different temperatures. The broken line demonstrates the start of the transformation paracelsian to celsian. The errors are smaller than the symbols.

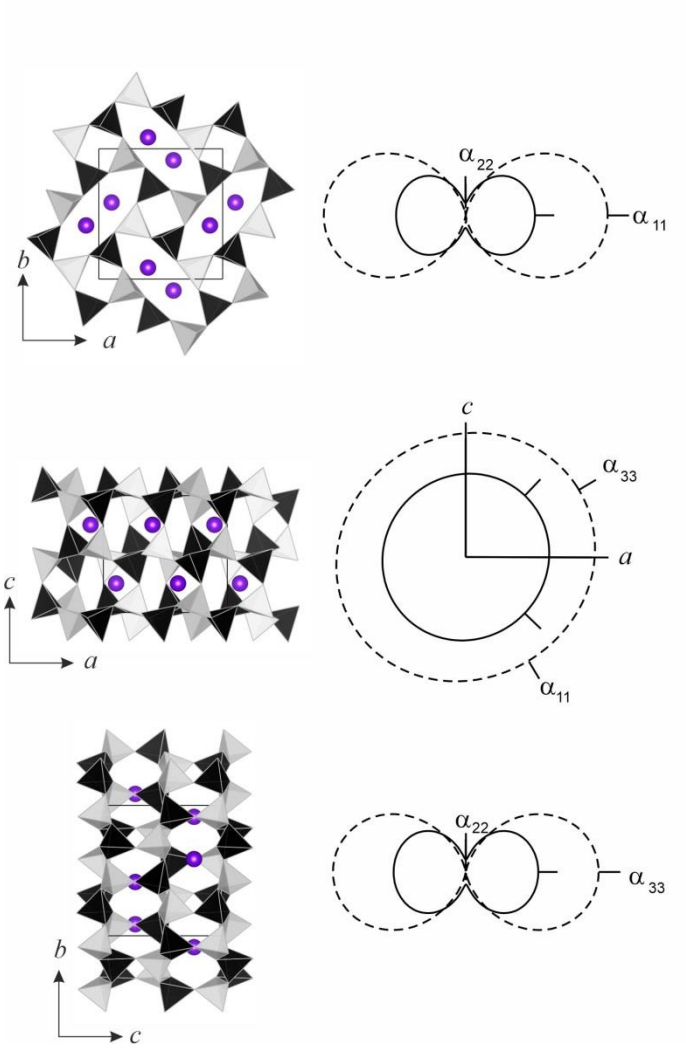

Fig. S3. Crystal structures of paracelsian with the section of the TECs figures. Solid and dashed lines indicate TEC figure section at 30 and 900 ºC, respectively. SiO_4 and AlO_4 tetrahedra are shown in grey and black, respectively, Ba atoms are shown as purple spheres.