Electronic supplementary information on JAAS-B909667A

Inter-correlation of impurity trace elements in bloodstone rock: X-ray fluorescence mapping studies

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S1. Quantitative analysis method

For determination of the distribution of elemental concentrations, the method basically same as Lachance-Traill algorithm [1] which has been successfully applied in material analysis [2, 3] was used to perform quantitative analysis. In the analytical process, the following three assumptions are used. The first is that the main chemical compositions are fixed at each scanning point and each point is considered as a flat, homogeneous and thick specimen. The second assumption is that beam intensity changes slowly during the entire scan and secondary fluorescence is neglected because of the low concentration of elements with higher atomic numbers and that the fluorescent element is associated with pure absorbers only. The third is that the composition of sample matrix is expressed as function of two components xFe and (1- x)SiO_2 where x is Fe concentration. Because Fe chemical states are different in different region of bloodstone , here we do not assume Fe_2O_3 and SiO_2 but Fe and SiO_2 as main components. Figure S1 gives a simple flow-chart of the quantitative analysis. According to assumptions mentioned above, the element fluorescence at each scanning point can be given by

$$p_i = qE_iC_i \int_{\lambda_0}^{\lambda_{abs,i}} \frac{\mu_{i,\lambda} I_\lambda d\lambda}{\mu_{s,\lambda} + \frac{\sin\psi_1}{\sin\psi_2}\mu_{s,\lambda_i}} \tag{1}$$

Where, p_i and E_i, are the integrated fluorescence intensity and excitation factor of the considered X-ray line for element i, respectively. C_i and I_λ are the concentration of element *i* and intensity of incidence X-ray. $\mu_{i,\lambda}$, $\mu_{s,\lambda}$ and $\mu_{s,\lambda i}$ are the absorption coefficient of element *i* for the incidence X-ray, the sample's main components for the incidence X-ray and the considered X-ray line for element *i*, respectively. q is defined as $q = \frac{\sin\psi_1}{\sin\psi_2} \times \frac{d\Omega}{4\pi}$ where Ψ_1, Ψ_2 and $d\Omega$ are the incidence angle, emergence angle and solid angle represented by the detector. Due to monochromic incidence X-rays in the synchrotron radiation facility, the equation described above can be reduced to

$$p_i = qE_iC_i \frac{\mu_{i,\lambda} I_\lambda}{\mu_{s,\lambda} + \frac{\sin\psi_1}{\sin\psi_2}\mu_{s,\lambda_i}} \tag{2}$$

Both standard samples and bloodstone are measured under the same experimental conditions (the incidence and emergence angle are 45°). So the intensity ratio of bloodstone and the standard samples for element i can be given by

$$\frac{p^i_{ST} / I_{\lambda_{in}}}{p^i_{BS} / I'_{\lambda_{in}}} = \frac{C^i_{ST}(\mu^{\lambda_{in}}_{BS} + \mu^{\lambda_i}_{BS})}{C^i_{BS}(\mu^{\lambda_{in}}_{ST} + \mu^{\lambda_i}_{ST})} \tag{3}$$

Where p^i_{ST}, and p^i_{BS} are the measured intensity for element i K_α in a standard sample and bloodstone, respectively and C^i_{ST} and C^i_{BS} are the concentrations of the corresponding element in a standard sample and bloodstone, respectively. $\mu^{\lambda_{in}}_{BS}$, $\mu^{\lambda_i}_{BS}$, $\mu^{\lambda_{in}}_{ST}$ and $\mu^{\lambda_i}_{ST}$ are the absorption coefficients of the standard samples and bloodstone for the incidence X-ray and the element *i*'s K_α. Table 1 shows the standard samples' major components , elemental concentration , absorption coefficient and measured integrated intensity for K_α of Rb, Sr in NIST 612 and Fe, Cu, and Zn in Glass beads. For NIST SRM 612, the major components and elemental concentration are derived from the certificate of NIST standard reference material. For Glass beads, the major components and elemental concentration are given by producer. The absorption coefficient is calculated from NIST physical reference data and 4 digital numbers were remained. Table 2 gives the calculated absorption coefficients for K_α of Fe, Cu, Zn, Rb, Sr and incidence X-ray with 19.5 keV in bloodstone in terms of concentration of Fe and SiO_2 where their values are defined as x and 1-x. For absorption coefficients, 2 digital numbers after point were remained. After putting the data given by Tables 1 and 2 into Equation (3), the relationship between elemental concentration and measured corresponding element K_α intensity in unknown bloodstone can be obtained by a simple calculation. The relationships between concentration and intensity for Fe, Cu, Zn, Rb, Sr in bloodstone are given by equations (4-8), respectively.

$$c_{Fe}^{m}(\%) = 4.879/(8.65\times10^{7}/p_{Fe}^{m} - 1.648) \tag{4}$$
$$c_{Cu}^{m}(ppm) = 1.024\times10^{-4}(37.17 + 292.8c_{Fe}^{m})p_{Cu}^{m} \tag{5}$$
$$c_{Zn}^{m}(ppm) = 7.8\times10^{-5}(32.18 + 257.52c_{Fe}^{m})p_{Zn}^{m} \tag{6}$$
$$c_{Rb}^{m}(ppm) = 2.40\times10^{-4}(12.326 + 109.52c_{Fe}^{m})p_{Rb}^{m} \tag{7}$$
$$c_{Sr}^{m}(ppm) = 2.53\times10^{-4}(10.4 + 48.89c_{Fe}^{m})p_{Sr}^{m}. \tag{8}$$

In equations (4-8), c and p are the concentration and measured integrated intensity for K_α of specific elements and the constants represent the product of the ratio of elemental concentration and measured corresponding elemental K_α intensity in a standard sample and the ratio of absorption coefficients for bloodstone and a standard sample. By using equations (4-8), the concentration of Fe, Cu, Zn, Rb and Sr in the desired region of bloodstone can be obtained. The errors of elemental concentration are mainly from statistical errors and are estimated to be less than 3.7% for Fe concentrations.

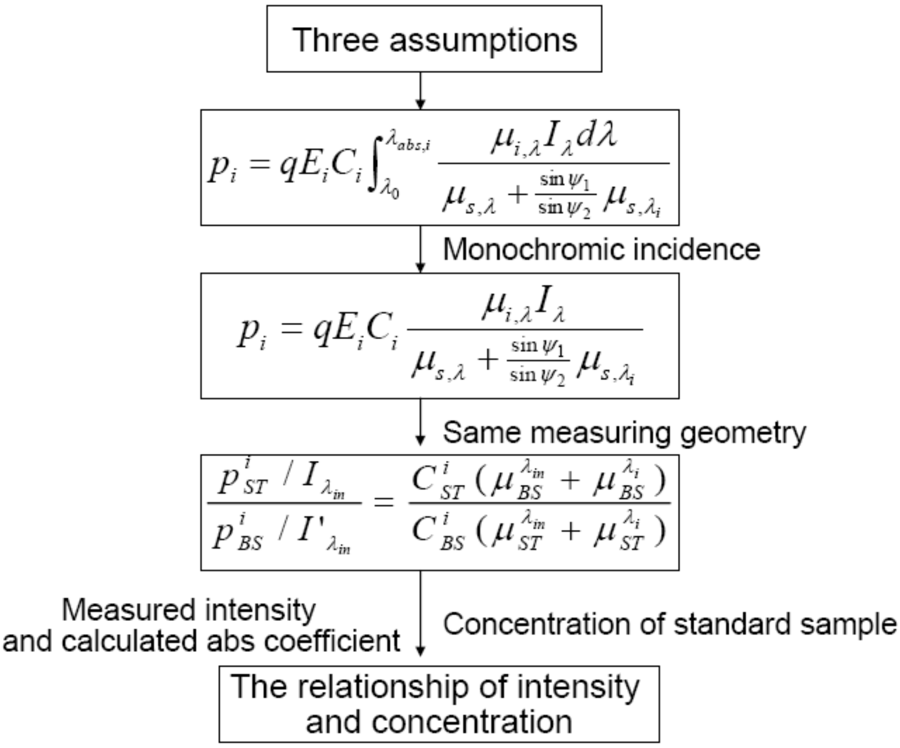

Figure S1 A flow-chart of the quantitative analysis.

Table 1 the major components, elemental concentration, absorption coefficient and measured integrated intensity for K_α of Rb, Sr, Fe, Cu and Zn in standard samples. NIST 612 sample's major components and elemental concentration are obtained from the certificate of NIST standard reference material. The Glass sample's major components and elemental concentration are given by producer. Absorption coefficients are derived from NIST physical reference data. The corresponding element's K_α intensity is the experimental value.

Standard sample	**Major components**	**Element i**	**Concentration for element i**	**Absorption coefficient for K_α of element i**	**Intensity for K_α of element i**
NIST 612	SiO_2 (72%) CaO (12%) Na_2O (14%) Al_2O_3 (2%)	Rb	31.4 ppm	12.79	970/300s
		Sr	45.8 ppm	10.24	1585/300s
Glass A	Li_4B_7 (90%) $LiCo_3$ (9.5%) KBr (0.5%)	Fe	100 ppm	12.08	1056/300s
Glass B		Cu	100 ppm	31.62	3405/300s
Glass C		Zn	100 ppm	27.46	50780/300s

Table 2 the bloodstone's absorption coefficient for K_α of Fe, Cu, Zn, Rb, Sr and incidence X-ray with 19.5 keV which are given in terms of the concentration of the sample's main components (Fe and SiO_2 are x and 1-x, respectively)

Energy	Fe K_α	Cu K_α	Zn K_α	Rb K_α	Sr K_α	19.5 keV
Absorption coefficient	73.98-0.53x	36.04+266.86x	30.82+231.58x	10.05+83.58x	8.01+22.95x	2.88+25.94x

Reference

1.G. R. Lachance and R. J. Trail, Can. J. Spec. 1966, 11, 43.
2. R. K. Srivastava, R. Chandra and A. Shastry, Proc. Indian. Acad. Sci. (Earth Planet. Sci), 2004, 113, 605.
3. V. A. Zartsev, T. A. Makarova, A.V. Bakhtiarov and L. N. Moskvin, Inorganic Materials, 2008, 14, 1559.

S2. X-ray fluorescence mapping

In the main text, X-ray florescence mapping on the bloodstone was discussed in detail. The followings are full color versions of Figures 3, 4 and 5.

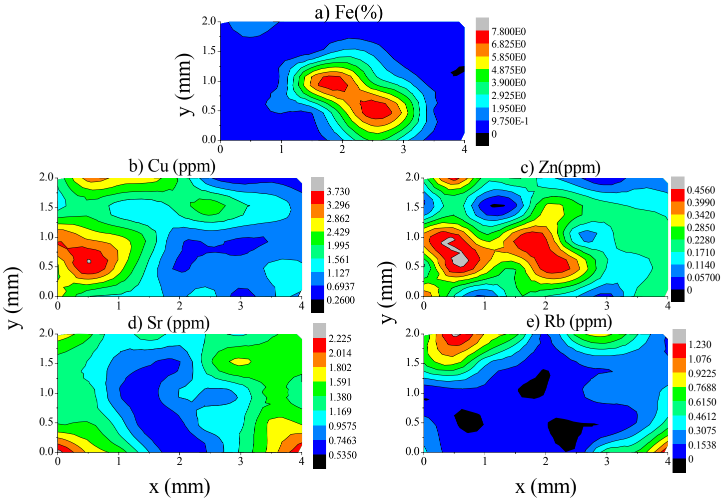

Figure S2
The distributions of Fe, Cu, Zn, Sr and Rb concentration transformed from integrated intensity of the XRF spectra for the region of interest of the bloodstone by using equation (1), where the unit is % for Fe and ppm for other elements. Fe Kα integrated intensity included the correction of sum peak when Fe intensity was high enough and Rb Kα integrated intensity was obtained from the sum peak of Rb Kα and Br Kβ by removing Br Kβ which is calculated by the ratio of Br Kα to Br Kβ when Br appeared (Full color version of Figure 3).

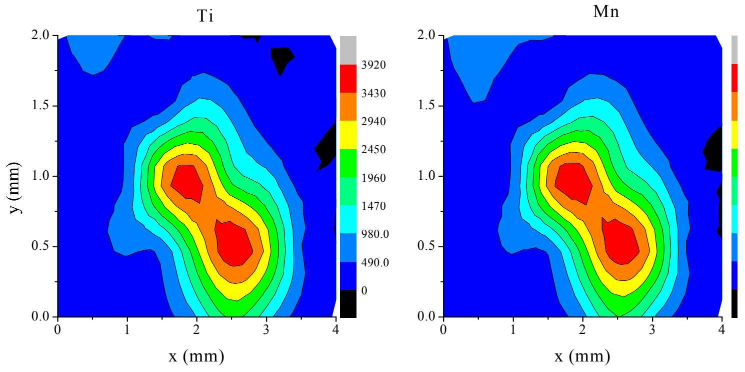

Figure S3
The distributions for K_α integrated intensity of Ti and Mn from XRF spectra corresponding to the region of interest of the bloodstone. The Mn integrated intensity is not net intensity but gross intensity because of high Fe K_α intensity (Full color version of Figure 4)..

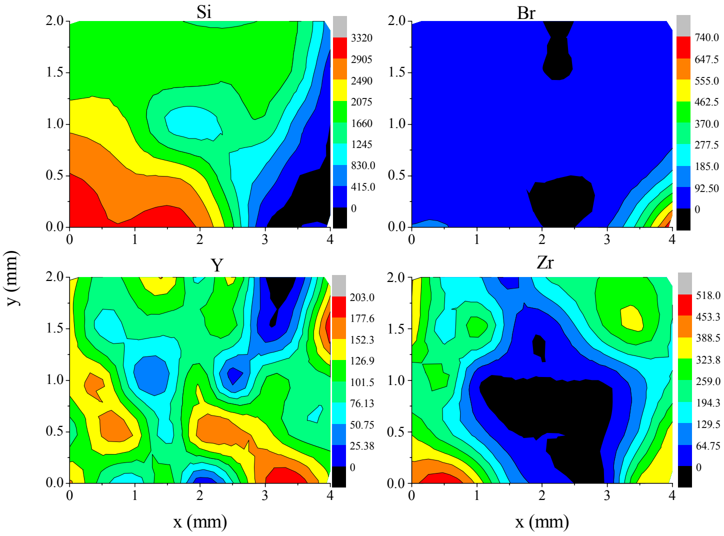

Figure S3

The distributions for K_α integrated intensity of Si, Br, Y and Zr from XRF spectra corresponding to the region of interest of the bloodstone. The integrated intensities of Y and Zr are obtained from the sum peak by removing Rb Kβ and Sr Kβ, respectively (Full color version of Figure 5).