doi:10.1017/S1431927621009090
Microsc. Microanal. 27 (Suppl 1), 2021

Elemental Mapping of Jade by pXRF and SEM-based Micro-XRF: A Comparative Study

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Jade objects are of interest to the heritage community given their significance to cultures in the ancient world. Jadeite ($NaAlSi_2O_6$) is a pyroxene mineral that represents the most rare variety of jade with only 19 known localities worldwide [1]. Some cultural heritage objects are suitable for vacuum chamber analysis in the laboratory by virtue of their smaller dimensions or robust nature with respect to low pressure. However for more delicate, or larger specimens, the use of a portable x-ray fluorescence spectrometer (pXRF) is the best option for rapid elemental identification, and this solution is suitable for field-, collections-, and gallery-based studies. In this study the relative spectral and imaging features of both pXRF and laboratory-based micro-X-ray fluorescence spectrometry (micro-XRF) coupled to a scanning electron microscope (SEM) are used to examine a Japanese jadeite-rich object (J1957) from the research collection of the Smithsonian's National Museum of Asian Art.

A Bruker Elio with a Rh source collimated to form an X-ray spot ≈ 1 mm was used along with a motorized stage to raster the analytical assembly to produce 2D elemental maps of a stationary object. X-ray images were collected using 50 kV and 75 mA of source current along with a 250 mm step size under ambient atmosphere. The laboratory-based micro-XRF measurements were collected using a Hitachi S-3700N SEM equipped with a Bruker XTrace equipped with a Rh source and a polycapillary optic capable of forming an X-ray spot of ≈ 33 mm (measured at Cu Ka). The XTrace was operated using 50 kV and 600 mA and a Bruker XFlash 6|60 SDD was used to collect X-rays. Given the XRF beam is fixed, micro-XRF mapping was performed by rastering the specimen using a Bruker Rapid stage (a piezo stick-slip XY substage assembly that couples to the SEM stage) with a dwell time of 4 ms per pixel. Quantification of extracted spectra from regions of interest of the hyperspectral micro-XRF map were performed using fundamental parameters (FP) implemented in Bruker Esprit v2.1 [3]. Energy dispersive spectrometry (EDS) maps using the electron beam in variable pressure (50 Pa) were also collected using the Rapid stage allowing for co-location with X-ray images generated by the XRF system.

In comparing the sum spectra from both pXRF and micro-XRF, the major difference between the two techniques is the reduced x-ray fluorescence signal for Na, Mg, Al, and Si in pXRF spectrum caused by the atmospheric adsorption of these lower energy photons when using pXRF (Figure 1) [3]. Despite the diminished Na, Mg, Al, and Si signals, the composite Cr, Fe, and Ca pXRF maps show similar compositional contrast to the micro-XRF images, albeit at differing spatial resolutions (Figure 2A, 2B). Specifically, micro-XRF is capable of mesoscale examination at a microscale resolution. The Ca-rich regions have a composition that is likely prehnite and regions enriched in Fe correspond to omphacite ($(CaNa)(Mg, Fe^{2+}, AlSi_2O_6)$, a pyroxene mineral often found in association with jadeite. Though, Ni and Sr are only present at trace concentrations in both omphacite and jadeite, both elements are enriched in omphacite by approximately a factor of 25 and 7.5 respectively. Unsurprisingly, the improved spatial resolution of micro-XRF offers additional details about the specimens including cross-cutting veinlets revealing the relative history of fluid deposition (Figure 2B). The improved resolution also allowed for the smaller Ba rich feldspar features to be resolved (Figure 2C). Another advantage of micro-XRF is the ability to map the Mg difference between omphacite and jadeite. Using the spectra from overall mapped area and the regions of interest pertaining to jadeite and omphacite (shown in Figure 2C), the quantified FP results, the calculated pyroxene cation site occupancy, and trace element concentrations are tabulated in Table I [2]. Given that the X-rays are emitted from 10s to 100s of micrometers from within the sample, the quantification will be further discussed in relation to X-ray depth of generation [3]. Additionally, comparison of the quantified micro-XRF and EDS results from the rapid stage maps will be presented, including an assessment of the accuracy of the quantification [5].

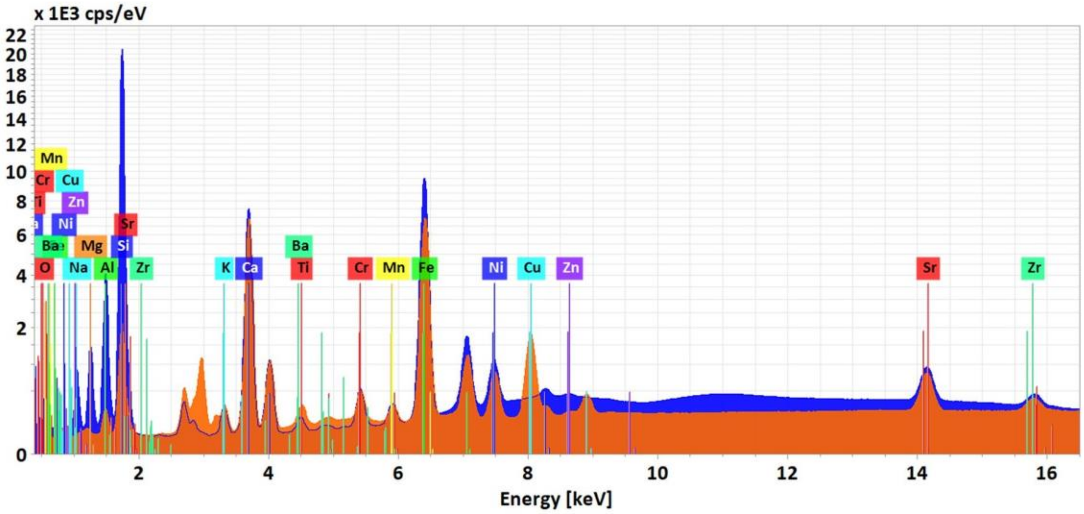
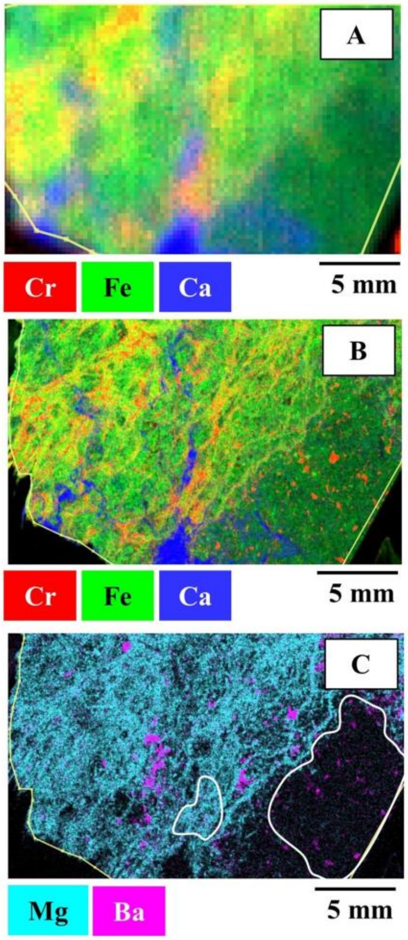


Figure 1. Micro-XRF sum spectrum (in blue) and p-XRF sum spectrum (in orange) for J1957 sample. Both spectra were normalized to Ca.



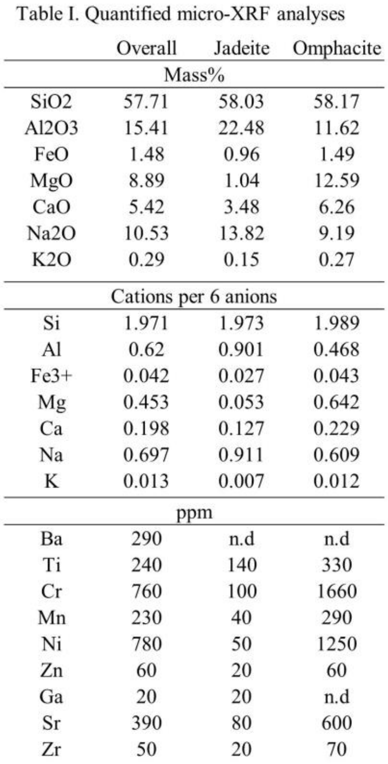


Table I. Quantified micro-XRF analyses

	Overall	Jadeite	Omphacite
	Mass%		
SiO2	57.71	58.03	58.17
Al2O3	15.41	22.48	11.62
FeO	1.48	0.96	1.49
MgO	8.89	1.04	12.59
CaO	5.42	3.48	6.26
Na2O	10.53	13.82	9.19
K2O	0.29	0.15	0.27
	Cations per 6 anions		
Si	1.971	1.973	1.989
Al	0.62	0.901	0.468
Fe3+	0.042	0.027	0.043
Mg	0.453	0.053	0.642
Ca	0.198	0.127	0.229
Na	0.697	0.911	0.609
K	0.013	0.007	0.012
	ppm		
Ba	290	n.d	n.d
Ti	240	140	330
Cr	760	100	1660
Mn	230	40	290
Ni	780	50	1250
Zn	60	20	60
Ga	20	20	n.d
Sr	390	80	600
Zr	50	20	70

Figure 2. J1957 (A) p-XRF (B) Micro-XRF (C) Micro XRF. Table of quantified of FP results from micro-XRF.

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[5] We acknowledge Freer Gallery of Art for access to J1957 with additional thanks to Janet Douglas (MCI emeritus).