Determination of Major, Minor, and Trace Elements in Jadeite using Scanning micro-X-ray Fluorescence

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Jade is found as a lithic archaeological artifact with principal sources in Asia and Mesoamerica. One variety is comprised of jadeite ($NaAlSi_2O_6$) and was valued by prehistoric artisans for both its visual and physical properties [1]. In this study, we have examined a bulk specimen from Japan (J1957) that has been cut, ground, and polished flat on one face [2].

A Bruker M4 Tornado scanning micro-XRF equipped with a Mo (collimated to 1 mm) and Rh (polycapillary tube with a 20 um spot at Mo K_α) x-ray sources, was operated at 50 kV for spectroscopic imaging. X-ray fluorescence was collected using two opposing 60 mm^2 silicon drift detectors (SDD). The irregularly shaped specimen was pressed into modeling clay with the aid of hand press, to maintain a near zero degree tilt of the polished face before being examined under vacuum.

An overview of the compositional imaging and associated spectra of J1957 reveals that some trace elements can be imaged without significant interference arising from x-ray diffraction (Fig. 1). Apart from increasing x-ray throughput, the dual detector geometry reduces the magnitude of such diffraction artifacts. Despite the thin architecture of the SDD, a few hundred μm in thickness, both Sn and Ba K lines were observed, above 25 and 32 keV respectively. Detection of these peaks was unexpected owing to the diminished quantum efficiency of the SDD at these high energies coupled with their low concentration in the specimen.

A subset of the specimen was imaged at higher spatial resolution revealing Cr, Mn, Ni, Mg, and Ca enrichment in veins (Fig. 2 A-D). Among the initial chemical phases identified by multivariate statistical processing were two that matched the major element atomic proportions of jadeite. These two phases were combined and reprocessed. The FP results for jadeite compare favorably to the major and minor compositions determined by standards-based electron beam analysis (Table 1), particularly given the large difference in volume the two analyses represent. Moreover, the μXRF cation proportions on the basis of 6 oxygens are equivalent to the electron beam result. The most significant difference is with respect to Mg, where the μXRF reports a zero concentration compared to 1.4 wt % by EPMA. Upon inspection of the XRF spectrum, the Mg detection limit is not the issue, but rather an overestimate of the Rh scatter background. Five elements are reported at the 10s of ppm level (Mn, Ni, Sr, Zr, and Ba), some with spectral overlaps (Fig. 3 A,B). With such sensitivity for trace elements, their ratios offer a potential tool for heritage scientists to test jadeite provenance. While previous trace element studies of jadeite employed locally destructive methods, e.g. laser ablation ICP-MS [2], μXRF is non-destructive, an important virtue for cultural heritage science [3].

References:
[1] F Lange, "Precolumbian jade: New geological and cultural interpretations," F Lange, editor (1993)
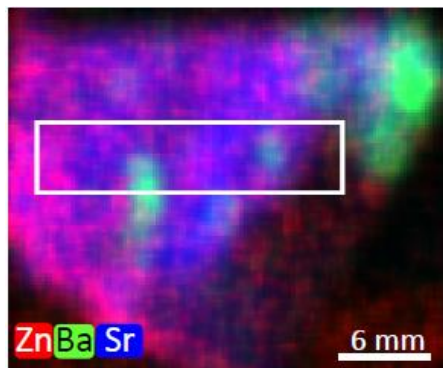[2] T Morishita et al, Island Arc **16** (2007), 40-56

Figure 1. Trace element image overview of jadeite fragment J1957 (Zn-red; Ba-green; Sr-blue) using a collimated Mo x-ray source and a step size of 250 μm.
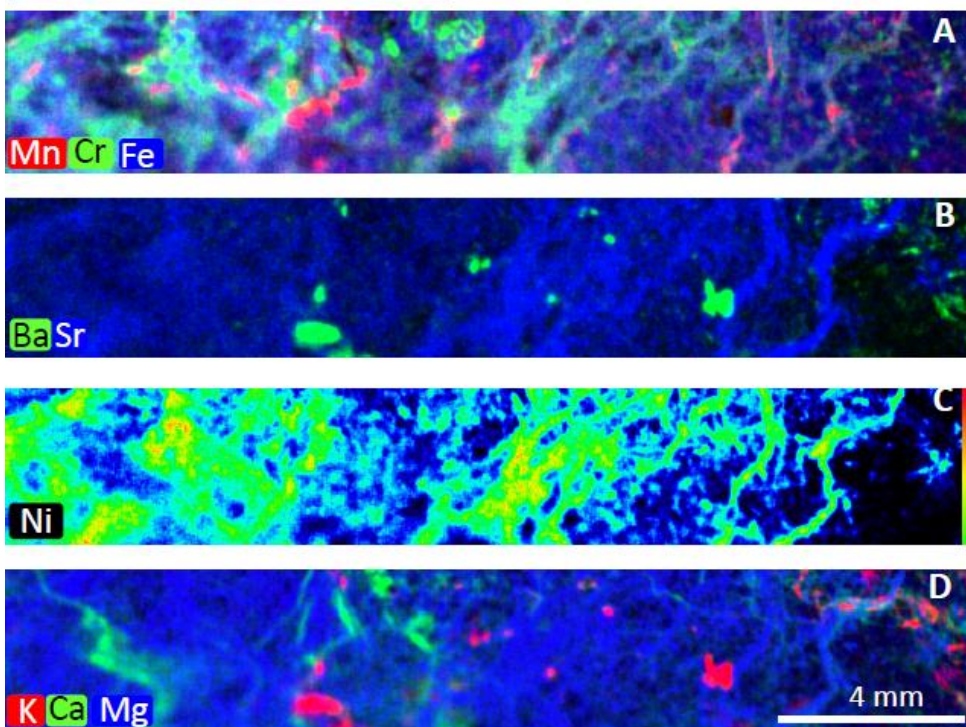

Figure 2. Minor and trace element image overlays using an unfiltered Rh x-ray source with a polycapillary optic and a step size of 15 μm. A) Mn-red; Cr-green; Fe-blue; B) Ba-green; Sr-blue; C) Ni-rainbow scale; D) K-red; Ca-green; Mg-blue.
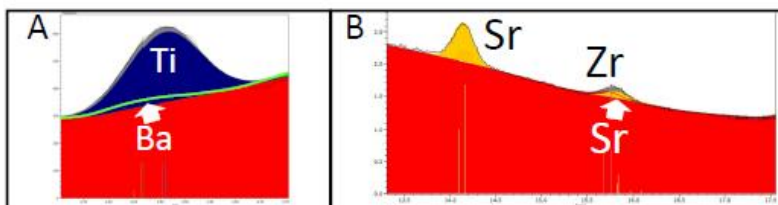

Figure 3. Graphical representation of spectral deconvolution of trace elements x-ray line interferences (red-x-ray scatter background; gray-fit spectrum). A) Ba L_α (37 ppm) on Ti K_α (132 ppm) at 4.5 keV; B) Zr K_α (13 ppm) on Sr K_β (87 ppm) at 15.8 keV.

Table 1. Quantitative jadeite analyses by FP-based μ XRF and standards-based electron beam EDS.

	μ XRF	e-beam
Avg. phase area		N=29
SiO_2	59.472	58.40
TiO_2	0.022	0.04
Al_2O_3	26.137	23.23
Cr_2O_3	0.021	0.04
FeO^*	1.010	0.76
CaO	3.353	1.79
MgO	0.000	1.37
Na_2O	14.774	14.60
Total	104.79	100.18
cations per 6 oxygens		
Si	1.939	1.981
Ti	0.001	n.d
Al	1.005	0.980
Cr	0.001	n.d
Fe^*	0.028	0.006
Ca	0.117	0.027
Mg	0.000	0.032
Na	0.934	1.001
total	4.024	4.029
ppm		
K	349	
Mn	27	
Ni	28	
Sr	87	
Zr	13	
Ba	37	