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Hyperspectral X-ray Analysis of Submicrometer-scale Heterogeneities in a Venerable Compositional Standard Provided by Nature: Kakanui Hornblende

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Among the most prominent features of the Kakanui breccia found on the south island of New Zealand are large hornblende xenocrysts (foreign crystals), some reaching more than a decimeter in length [1]. Because the atomic structure of hornblende is sufficiently complex, a wide range of cations can be readily accommodated into multiple crystallographic sites. Kakanui hornblende is more specifically kaersutite, a Ti- and Ca-rich amphibole whose ideal formula may be written:

$$Ca_2(Na,K)(Mg,Fe^{2+},Fe^{3+})_4Ti(Si_6Al_2)O_{22}(OH,F)_2 \quad [2]$$

The large crystal size, together with Kakanui hornblende's "cation soup," made it an ideal candidate for one of the first reference specimens characterized by Gene Jarosewich during his early years of research at the Smithsonian Institution [3,4]. This material has proven to be of great value to many by virtue of its use as a chemical standard in hundreds of published geological studies. Gene's careful wet chemical analyses, coupled with his EPMA homogeneity studies, provided the Earth and planetary science community with the best and largest set of like-standards for X-ray microanalysis of minerals and natural glasses. We have conducted a modern reexamination of Kakanui hornblende and have discovered fine-scale chemical heterogeneity invisible to Jarosewich and co-workers when they published their often cited Geostandards Newsletter paper in 1980.

An FEI Nova NanoSEM600 field-emission scanning electron microscope operated at 7 keV and a ThermoFisher Scientific NSS300 EDS analyzer were used to chemically image submicrometer-scale irregularities in the polished surfaces of Kakanui hornblende grains. Swarms of the observed inhomogeneities resemble melt inclusions, often with high average Z daughter crystals (Figure 1). The inclusions are enriched in Si, Na, Fe, and Al, and depleted with respect to Mg and Ca, relative to the host amphibole. Combined multivariate statistical (Compass/AXSIA) and XPhase (a routine that performs an N dimensional comparison of pixel intensities) analysis yields the location of all chemical phases as a series of binary masks (Figure 2). The data underlying all pixels in each mask can be used to extract derived spectra for each chemical phase, which when weighted by area fraction, can be used to compute the local bulk composition (Table 1). These chemical inhomogeneities in Kakanui hornblende account for some of the variance observed in trace element studies [5,6] and highlight the care that should be taken in using this material for a primary standard. Boundary phases in Figure 2 indicate the interaction volume is still too large to fully resolve the inclusions and STEM EDS is required to fully isolate their composition.

References

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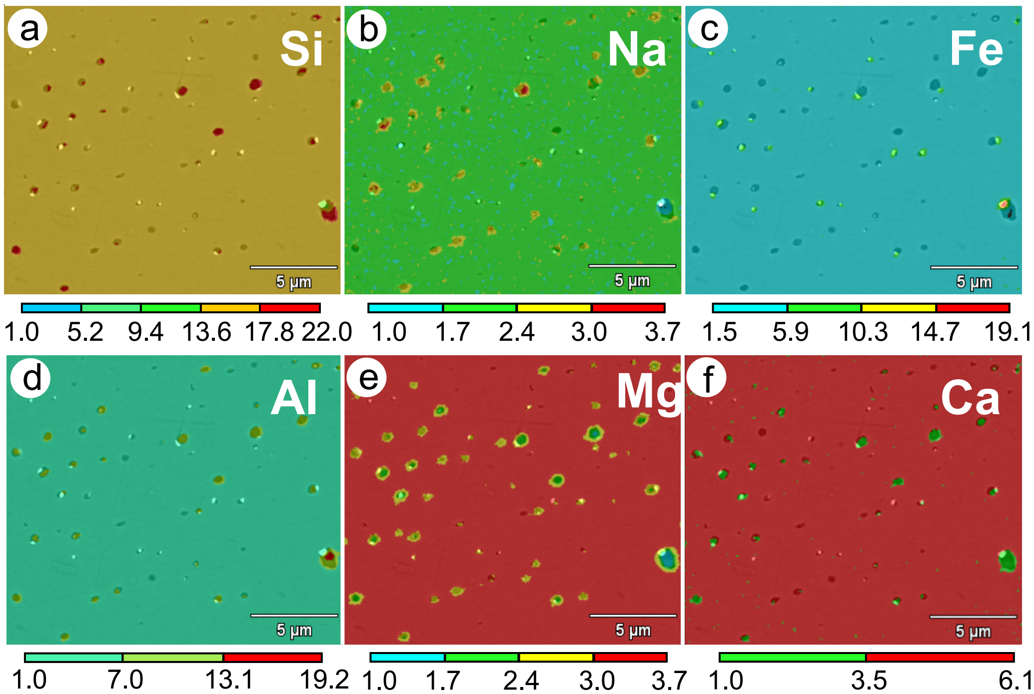

Figure 1. Quantified elemental images expressed as atom %.for hornblende standard with inclusion inhomogeneities. a-d) Si, Na, Fe, and Al are all enriched with respect to the host crystal, e,f) Mg and Ca are depleted relative to Kakanui hornblende.

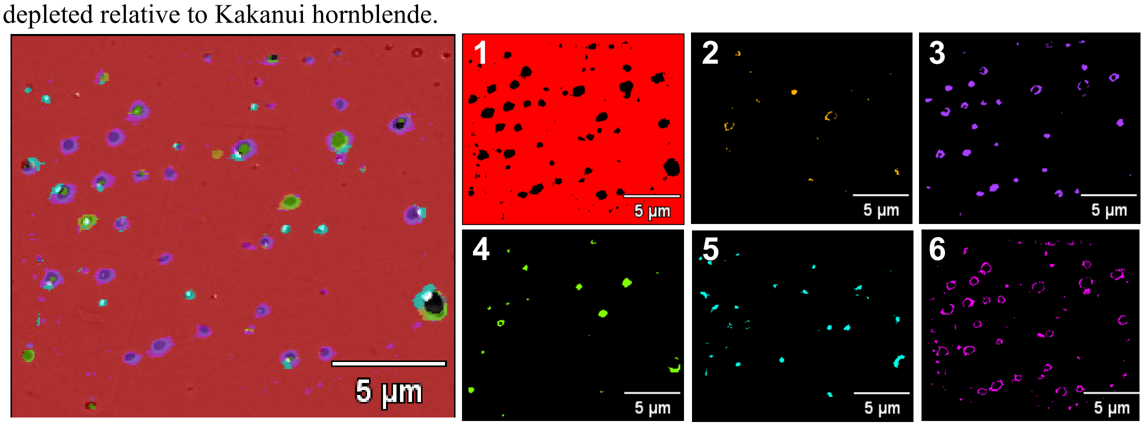

Figure 2. Left) Composite phase image. Right) Binary masks for 6 phases identified by MVS calculations and n-dimensional pixel comparison.

Table 1. Canonical values for the chemistry of Kakanui hornblende in comparison to the computed local bulk composition. The compositions of segmented phases and their area percentages (Fig. 2) are also listed.

	wet chemistry	**computed phase composition**	segmented phases 1	2	3	4	5	6
area (%)			93.9	0.7	0.3	0.8	1.8	2.1
SiO_2	40.37	**39.5**	39.5	47.8	42.2	36.9	42.3	39.9
TiO_2	4.72	**5.2**	5.2	3.5	4.4	5.6	4.2	5.1
Al_2O_3	14.9	**13.0**	13	16.6	14.2	12.6	14.6	13.4
FeO*	10.92	**13.7**	13.7	11.3	13.2	19.3	12.9	13.8
MnO	0.09							
MgO	12.8	**11.9**	12.1	7.2	10.2	10.4	9.8	11.3
CaO	10.3	**9.7**	9.8	6.6	9.2	8.9	8.6	9.6
Na_2O	2.6	**2.6**	2.6	3	2.6	2.5	3.4	2.9
K_2O	2.05	**2.0**	2.0	1.7	1.8	1.7	2.1	2.0
H_2O	0.94							
Total	98.75	97.6	98.7	98.8	98.8	98.8	98.7	98.7