Minerals from the Kakanui Volcanic Breccia: A 2017 Look at Geological Reference Materials for EPMA

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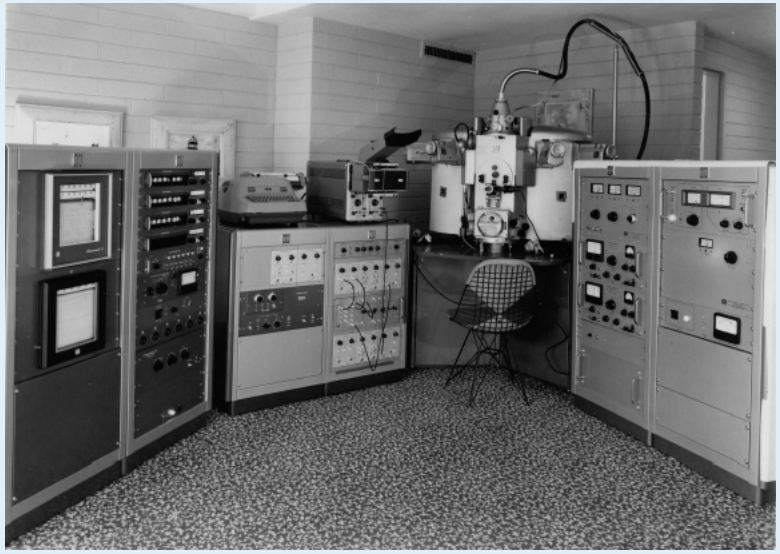
In 1960-70s there was an explosion of e-probes being built and sold. Many early applications had been in metals and alloys. As it became a tool of interest to geologists, the need for mineral and glass standards increased.



Gene Jarosewich and co-workers at the Dept of Mineral Sciences of the Smithsonian's Natural History Museum began a project to identify EPMA geological standards.

Today many labs use the USNM **Kakanui hornblende standard** which is distributed as NMNH 143965.

Eugene Jarosewich 1926-2007

There is common acceptance that this is **an excellent standard**, with all major and minor elements of interest in common silicate minerals and glasses.

Kakanui Megacrysts

PYROPE, AUGITE, AND HORNBLENDE FROM KAKANUI, NEW ZEALAND

BRIAN MASON

United States National Museum, Washington, D.C.

(Received for publication 17 January 1966)

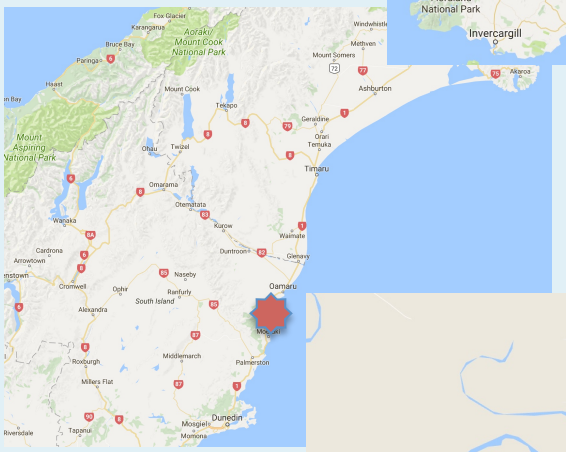
ABSTRACT

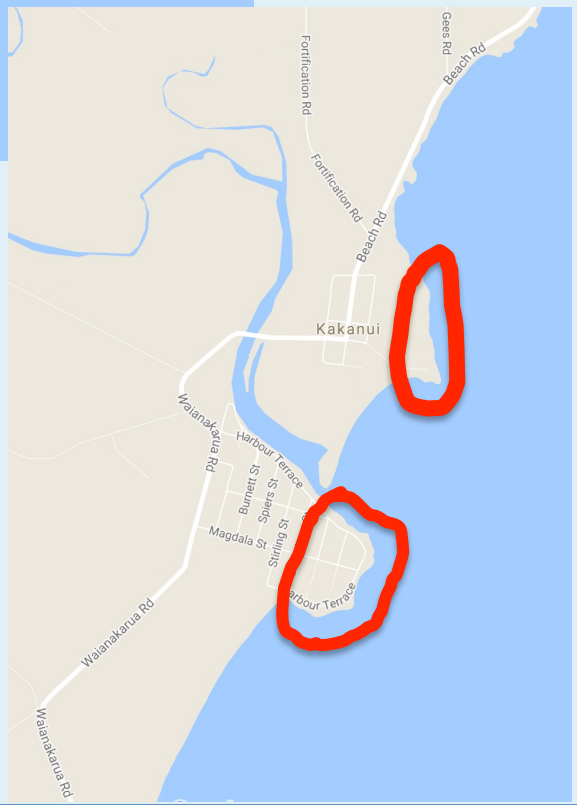
Pyrope, augite, and hornblende occur as xenocrysts in a volcanic breccia of Whaingaroan (Lower Oligocene) age at Kakanui. The pyrope has the composition $Py_{66.4}$ $Al_{20.0}$ $Gr_{10.9}$ $An_{2.1}$ $Sp_{0.6}$; $n = 1{\cdot}741$; $D = 3{\cdot}72$; $a = 11{\cdot}536$ Å. The augite is an aluminous variety with tschermakitic affinities; $\alpha = 1{\cdot}686$, $\beta = 1{\cdot}691$, $\gamma = 1{\cdot}713$; optically positive, $2V = 55°$; $D = 3{\cdot}33$. The hornblende is a hastingsite; $\alpha = 1{\cdot}676$, $\beta = 1{\cdot}687$, $\gamma = 1{\cdot}695$; optically negative, $2V = 80°$; $D = 3{\cdot}22$. The occurrence and associations of these minerals suggest that they originated in the upper mantle.

INTRODUCTION

In 1936 Professor Allan took a group of his students on a field trip to the Oamaru district during the August vacation—a trip I still remember with much pleasure and appreciation. Although the emphasis was on stratigraphy and paleontology, we spent some time examining the remarkable mineral breccia outcropping on the coast immediately north and south of the mouth of the Kakanui River. I have revisited this locality several times

The mineral breccia forms the extremities of Kakanui North and South Heads. The breccia itself is of limited extent at each of these localities and grades laterally into submarine tuffs. This is the Deborah Volcanic Formation of Gage (1957), and the stratigraphy and paleontology indicate a Whaingaroan (Lower Oligocene) age. The location of the two outcrops of mineral breccia suggest that they are marginal to a diatreme whose centre probably lies a short distance out to sea off the mouth of the Kakanui River.



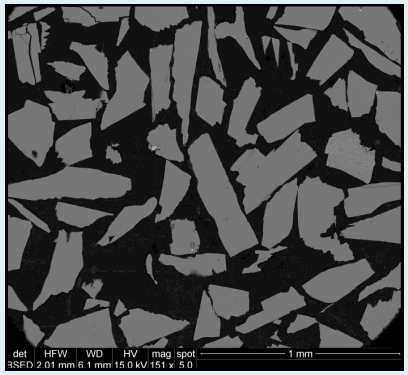


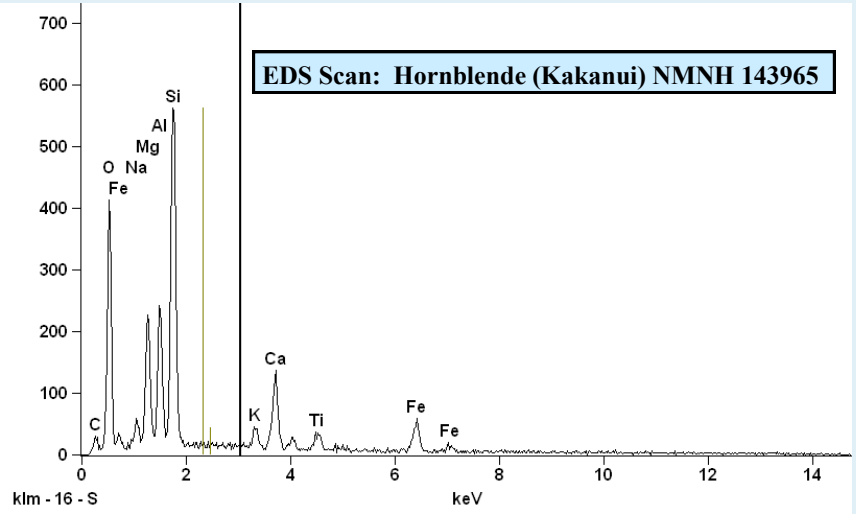
Smithsonian
National Museum of Natural History

On: mineralsciences.si.edu/facilities/standards/datasheets

Hornblende (Kakanui) NMNH 143965

SiO_2:	40.37
Al_2O_3:	14.90
Fe_2O_3:	3.30
FeO:	7.95
MgO:	12.80
CaO:	10.30
Na_2O:	2.60
K_2O:	2.05
TiO_2:	4.72
P_2O_5:	0.00
MnO:	0.09
H_2O:	0.94
TOTAL	100.02





Analyst: E. Jarosewich (Jarosewich *et. al.*,1980)

Source: Kakanui, New Zealand

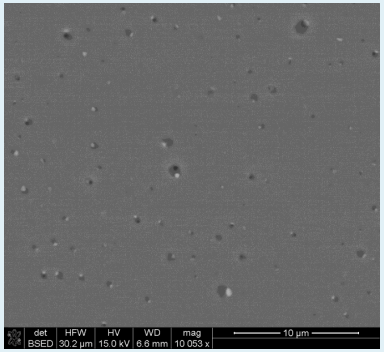
Sizes available:

0.590 mm - .420 mm,
> 0.420 mm
0.420 mm - 0.297 mm
0.420 mm - 0.250 mm
0.297 mm - 0.177 mm
0.250 mm - 0.177 mm
0.250 mm - 0.177 mm
0.177 mm - 0.125 mm

Standard Specifics:

Impurities: FeTi oxide: complex melt (?) inclusions with tiny oxide crystals; abundant (see image)

Impurities: FeTi oxide: larger individual crystals; rare



References:

Jarosewich, E (1972) Chemical Analysis of Five Minerals for Microprobe Standards. *Smith. Contr. Earth. Sci. 9, p. 83-84.*

Jarosewich, E., Nelen, J. A., and Norberg, J. A. (1980) Corrections. *Geostandards Newsletter 4, p. 257-258.*

Jarosewich, E., *et. al.* (1980) Reference Samples for Electron Microprobe Analysis. *Geostand. Newslett. 4, p. 43-47.*

Jarosewich, E., *et. al.* (1979) Microprobe Analyses of Four Natural Glasses and One Mineral: An Interlaboratory Study of Precision and Accuracy. *Smith. Contr. Earth. Sci. 22, p. 53-67.*

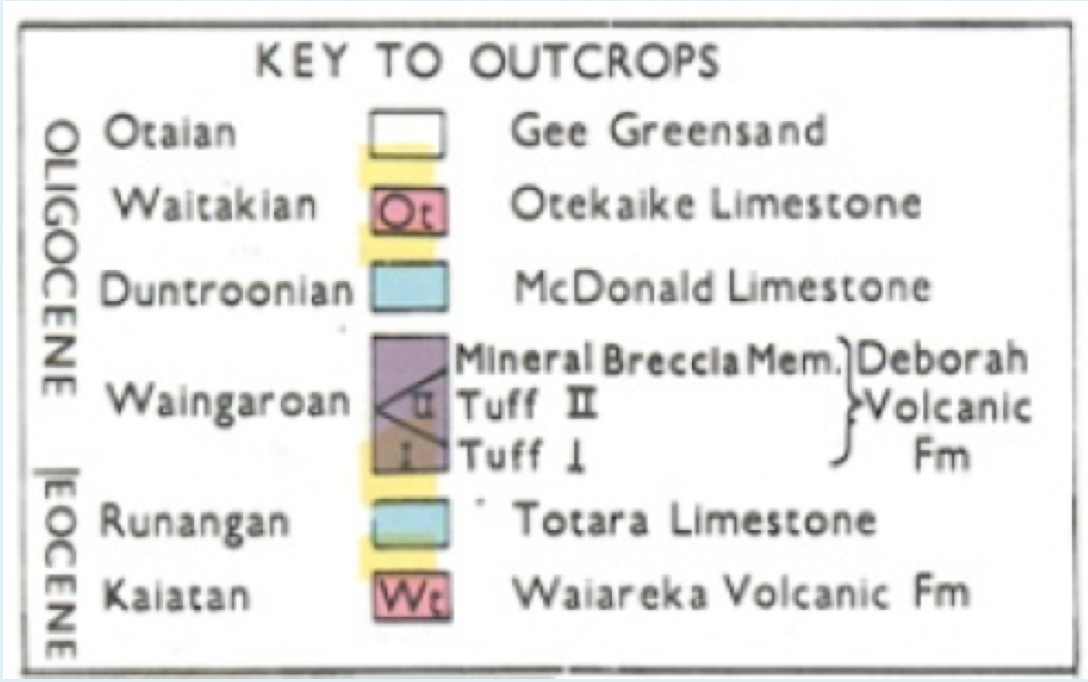
Mason, B. (1966) Pyrope, augite and hornblende from Kakanui, New Zealand. *J. Geol. Geophys. 9 (4), p. 474-480.*

Motivation: If Kakanui minerals are megacrysts, might it be possible to locate larger standards?

- Reduce the problems/difficulties mounting and polishing (and repolishing)
- Reduce need for relocating points on many small grains (to get 5-10 analyses to average)

And what better place to go in January than New Zealand!

Kakanui Outcrops



Dickey, 1968, Observations on the Deborah Volcanic Formation Near Kakanui, New Zealand, New Zealand Journal of Geology & Geophysics, 11, 1159-62

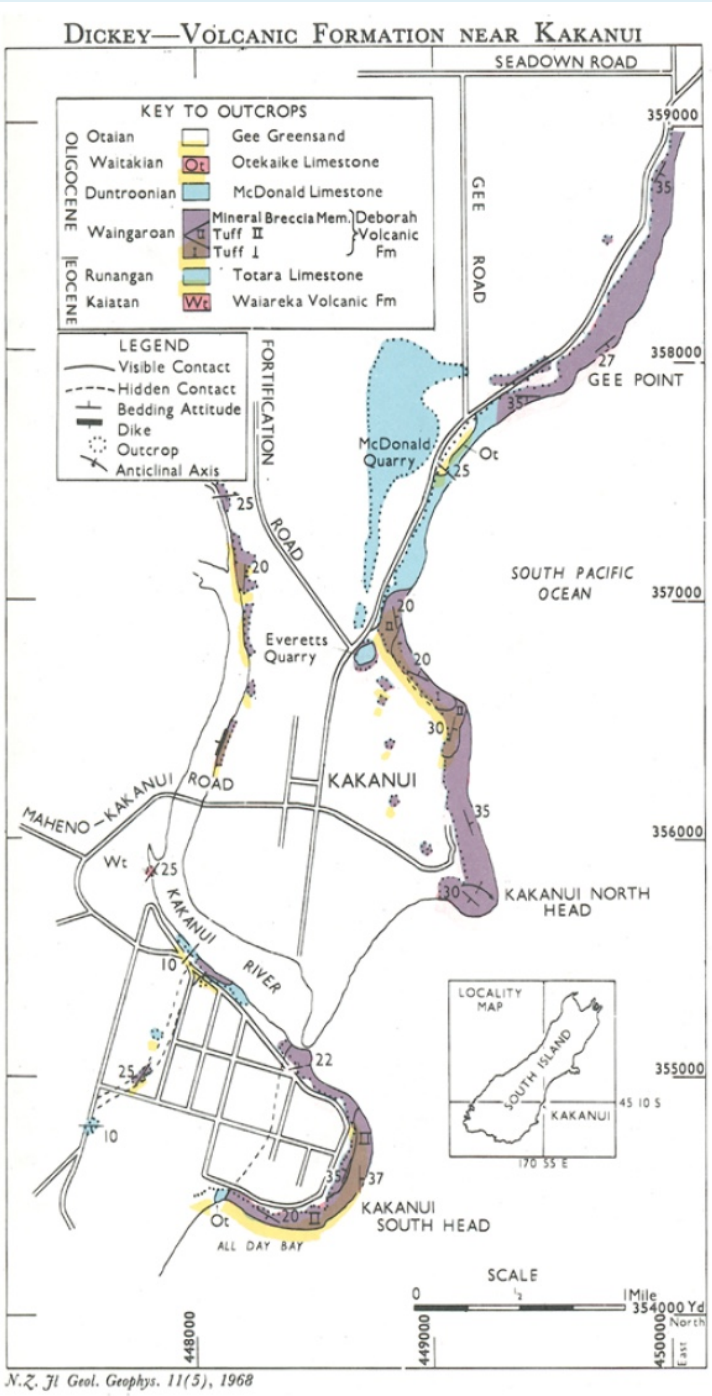


FIG. 1—Map showing rock outcrops at Kakanui.

South Head, Kakanui

High Tide 5:36 PM

Low Tide 9:14 AM…very slippery

Tide Coming in 3:09 PM

North Head, Kakanui

High Tide, 6:47 pm

North Head, 12:52 pm

North Head, Kakanui

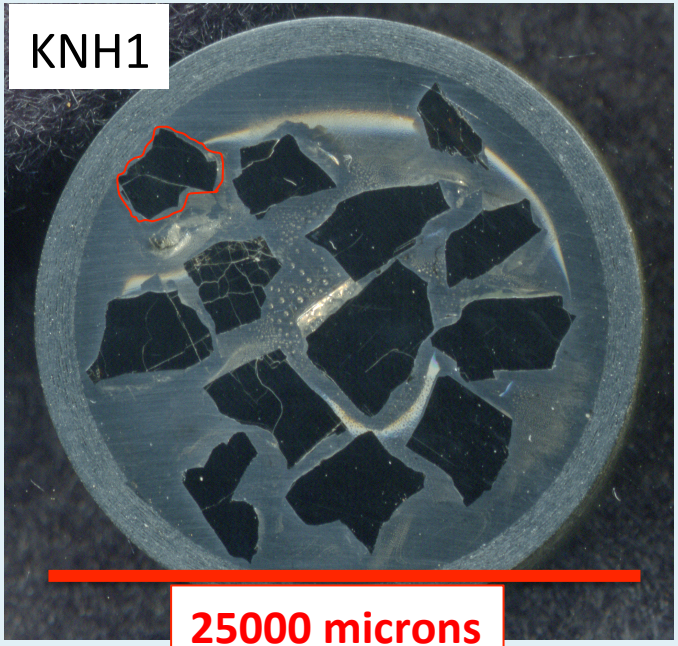
Tide out 1:05 PM

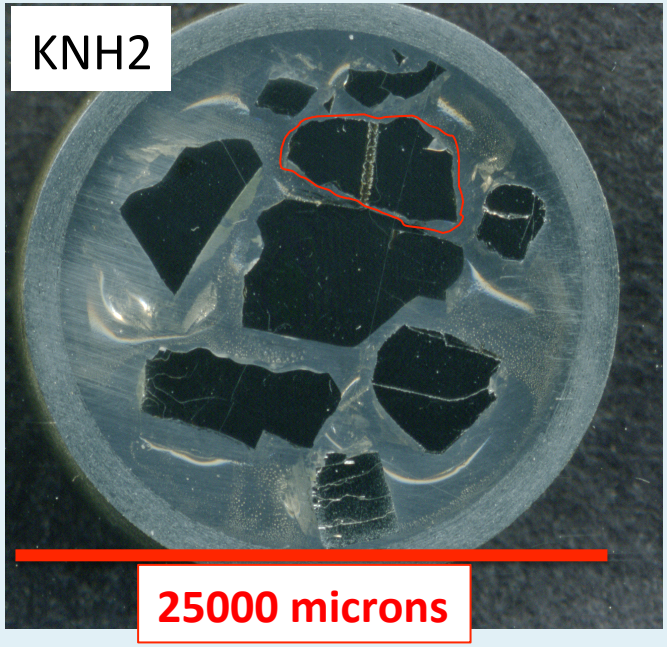
Tide out 12:52 PM

North Head Tide Out 1:33 PM

Acres of hyloclastite: welded subaquous volcanic flows. Indurated. Extremely cemented.

Serendipitous Kakanui Hornblende (North Head)





Augite

Size of grains of NMNH Kak Hb in UW std mount

Tiny Inclusions in the Kakanui Hornblendes – Investigated by Vicenzi and Rose (2008)

522
DOI: 10.1017/S1431927608089137

Microsc Microanal 14(Suppl 2), 2008

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

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* Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560-0119
** Surface and Microanalysis Science Division, NIST, Gaithersburg, MD

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:

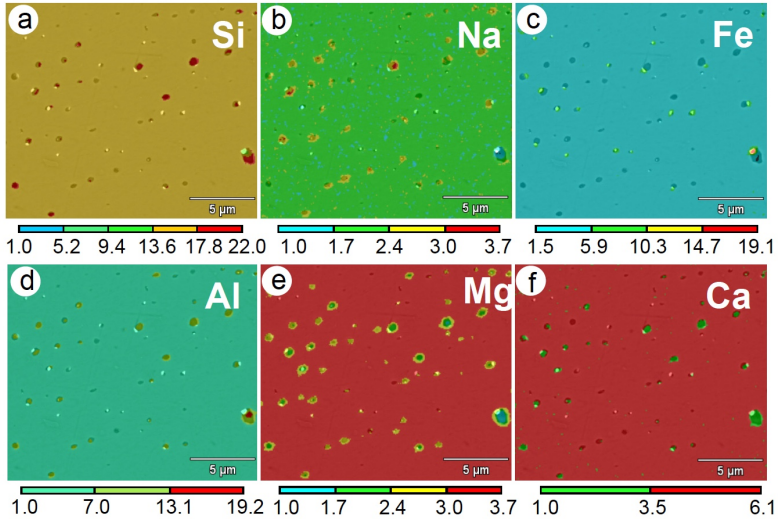
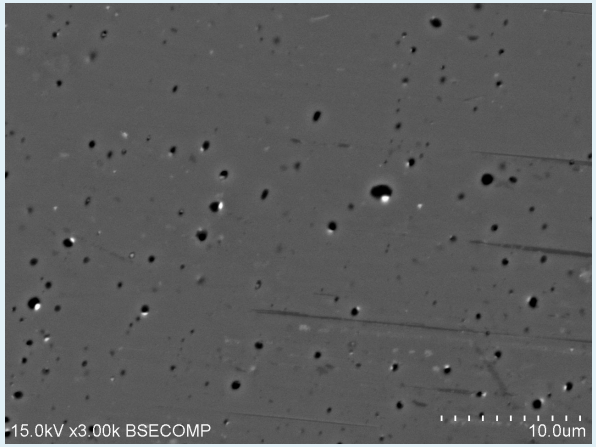
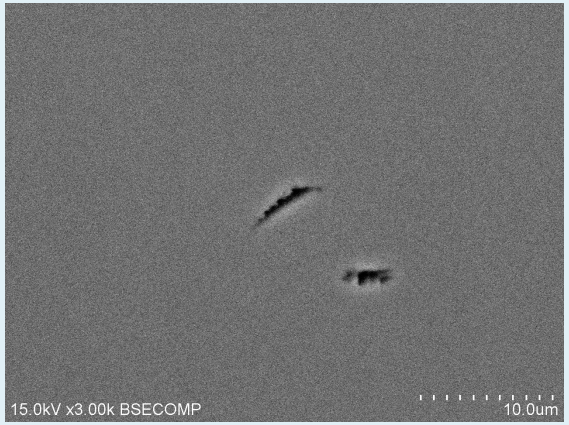


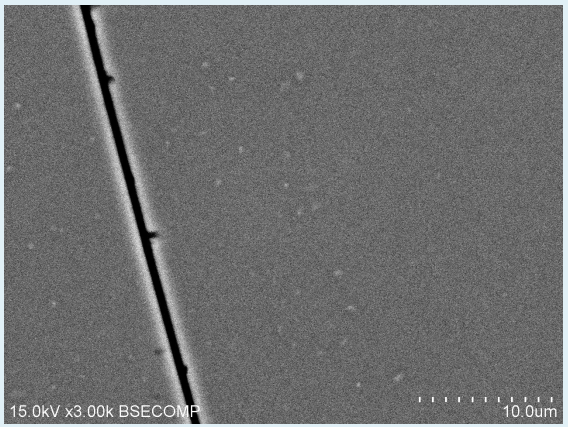
Figure 1. Quantified elemental images expressed as atom %.for hornblende standard with inclusion inhomogeneities. a-d) Si, Na, Fe, and Al are all enriched with respect to the host crystal, e,f) Mg and Ca are depleted relative to Kakanui hornblende.

Inclusions in the 2017 Kakanui Hornblendes?

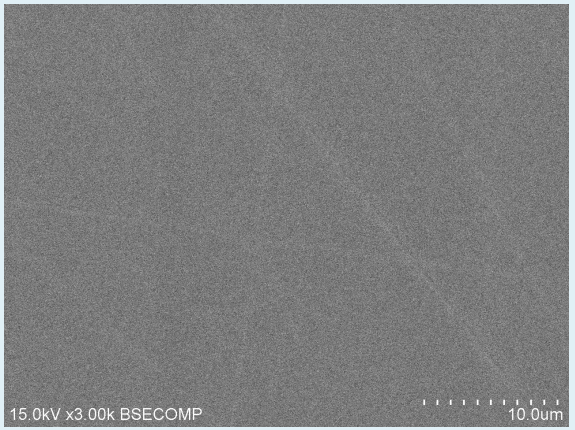


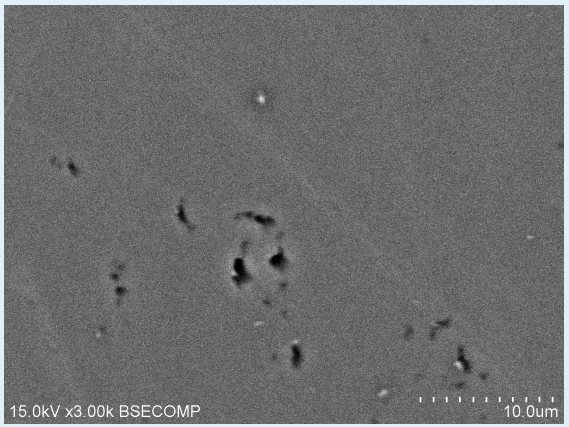
NMNH Kakanui Hornblende in UW std mount: micron vapor+Fe oxide inclusions (pretty uniformally distributed)





KHN2-Grain 1





KHN2-Grain 2

Compositions of Kakanui Hornblende ("Kaersutite")

767 analyses from 20 grains
30-40 points per grain

Other published values

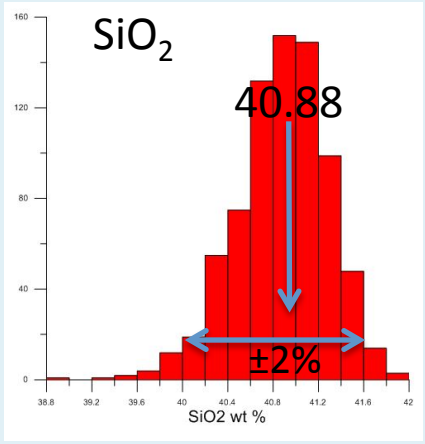
	(this study)		NMNH	Reay et al, 1989	
	KNH 2017	rsd	143965	KK2	KK1
SiO2	40.88	0.40	40.37	40.55	40.33
TiO2	5.02	0.08	4.72	4.91	5.75
Al2O3	15.39	0.13	14.90	14.96	14.63
FeO	9.12	0.18	10.92	9.56	9.61
MgO	13.48	0.14	12.80	13.60	13.22
CaO	10.37	0.10	10.30	10.27	10.03
Na2O	2.39	0.07	2.60	3.29 ?	2.57
K2O	2.16	0.05	2.05	2.22	2.12
Sum	98.81		98.66	99.36	98.26

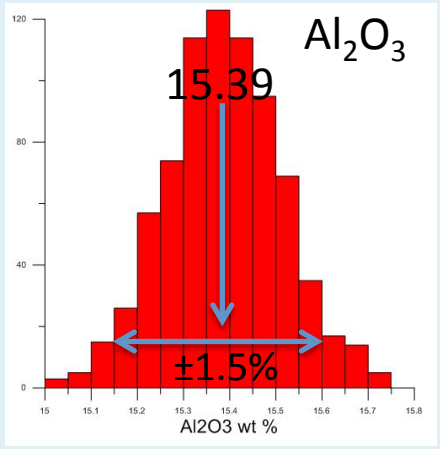
15 kV, 20 nA, 10 um beam,
10 second counts, MAN bkgs

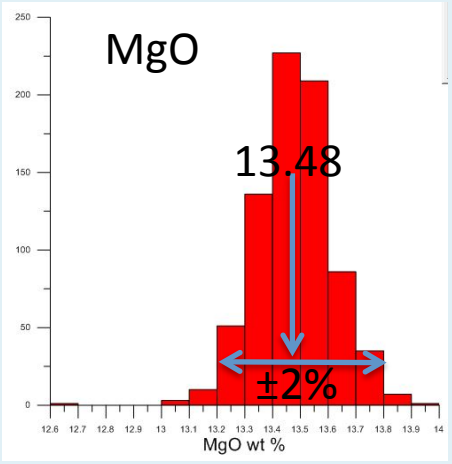
Smithsonian, published composition

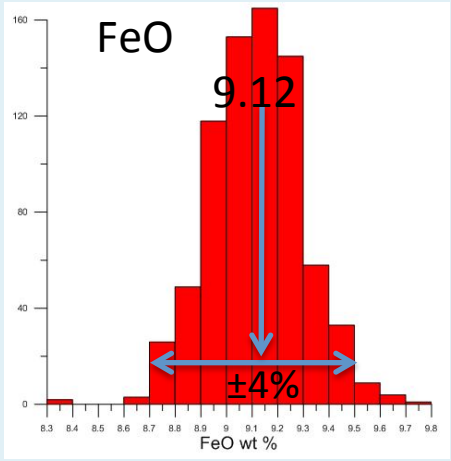
Reay, Johnsone and Kawachi, 1989, Kaersutite, a posssible international microprobe standard, Geostandards Newsletter, 13, 187-190.

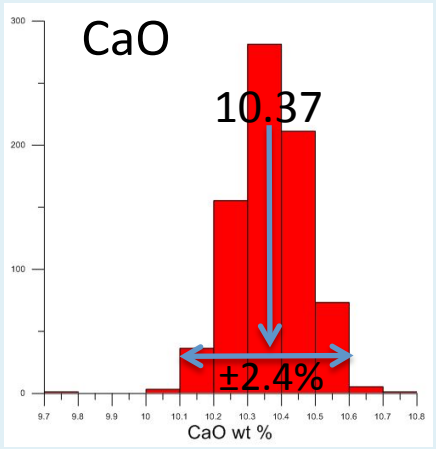
Histograms: 767 analyses of 20 grains

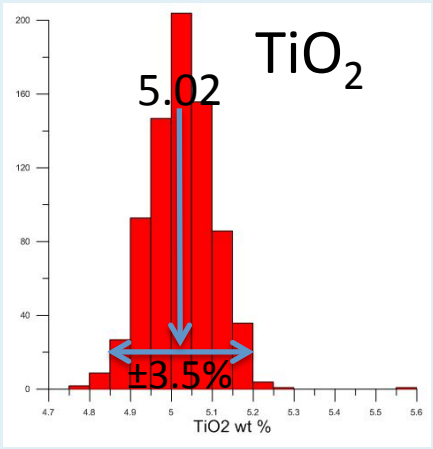


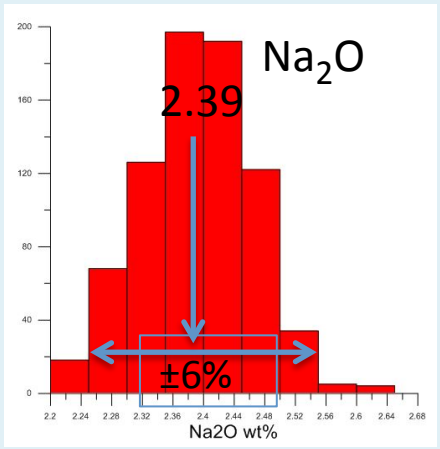


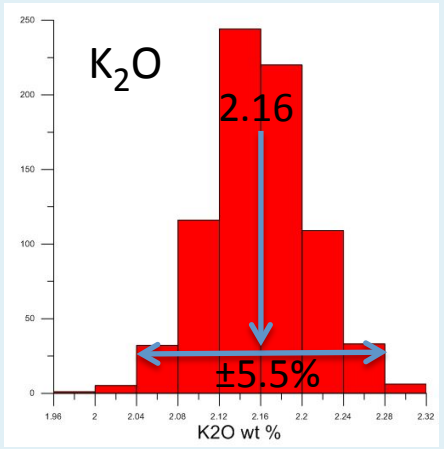










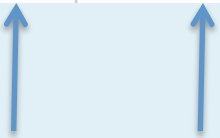


Homogeneity calculations using the Boyd et al. criterion

$$\text{Sigma ratio for 10 grains} = \frac{\text{observed sigma for all grains}}{\text{sigma predicted from counting statistics}}$$

$$\text{Sigma ratio for least homogeneous grain (in parentheses)} = \frac{\text{observed sigma for this particular grain}}{\text{sigma predicted from counting statistics}}$$

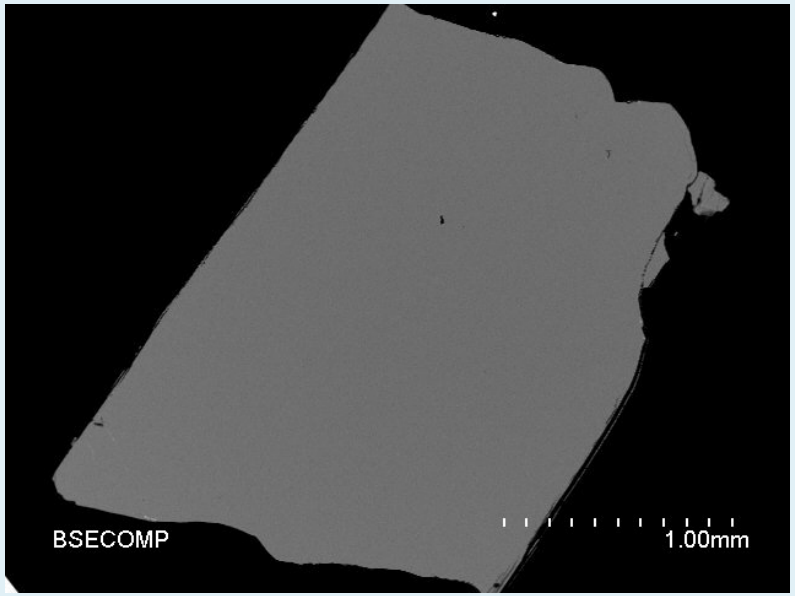
	NMNH	143965		Kakanui NorthHead Mount 2				
	10 grains	least homog	grain 2	grain 5	grain 6	grain 7	grain 4	grain 8
Si	1.01	1.38	2.05	2.18	1.94	2.53	2.44	1.72
Ti	1.01	1.49	0.99	1.08	0.85	1.04	1.32	1.18
Al	1.00	1.24	0.91	0.88	1.07	1.95	1.00	1.11
Fe	1.30	1.67	0.92	0.98	1.26	0.54	0.94	1.10
Mg	1.16	2.38	0.97	0.97	0.93	1.41	0.82	1.48
Ca	1.10	1.73	1.20	0.90	1.07	1.18	1.10	1.26
Na	1.15	2.15	0.78	1.03	1.22	1.22	0.92	1.00
K	0.90	1.29	1.10	1.22	1.38	1.04	1.14	1.16



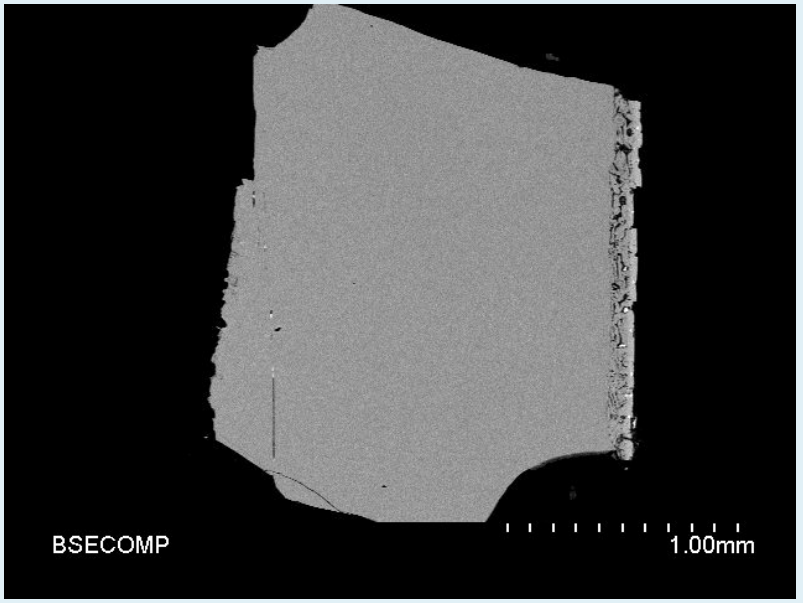
From Jarosewich et al., 1980

Boyd, Finger and Chayes, 1967, Computer reduction of electron-probe data, Carnegie Institution Year Book, 67, 210-215.

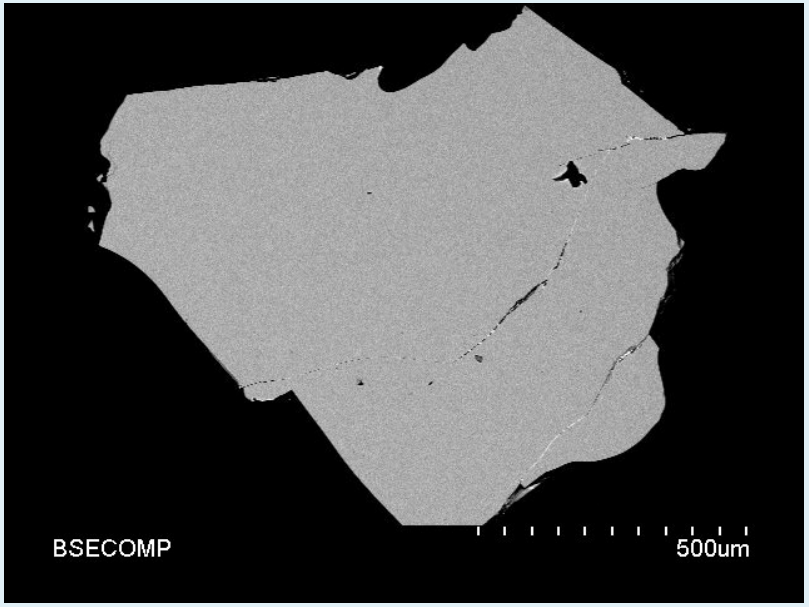
Other 1-2 mm Grains from Kakanui Megacrysts (U. Otago collection)



Kakanui Anorthoclase – from James Scott



Kakanui Augite – from James Scott



Kakanui Pyrope – from James Scott

Summary

1. There are large crystals in the Kakanui breccia which may be useful for geological EPMA reference materials ("standards"). Hornblende from a large hyloclastite block collected in early 2017 shows promise.
2. These crystals need to be further characterized, and the MAS Standards FIG is the logical entity to help organize this.
3. Ultimately, if they pass muster (#2 above), one idea would be to cut into 1-2 mm slabs and cut into 3-4 mm squares, which could be distributed.
4. There may also be megacrysts in the Smithsonian collections which should be examined.