

1 **Revision 6**

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3 **Ferri-kaersutite, $\text{NaCa}_2(\text{Mg}_3\text{TiFe}^{3+})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$, a new oxo-**
4 **amphibole from Harrow Peaks, Northern Victoria Land, Antarctica**

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17 **Running title:** Ferri-kaersutite, a new oxo-amphibole
18

19 **ABSTRACT**

20 Ferri-kaersutite, ideally $\text{NaCa}_2(\text{Mg}_3\text{TiFe}^{3+})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$, is a new oxo-amphibole from Harrow
21 Peaks, Northern Victoria Land, Antarctica. It occurs as brown prismatic crystals, up to 200 μm in
22 length, with a vitreous luster, and a perfect $\{110\}$ cleavage. Ferri-kaersutite is associated with
23 forsterite, diopside, and Cr-bearing spinel. Chemical analyses, by a combination of electron
24 microprobe, SIMS, and ^{57}Fe Mössbauer spectroscopy, gave the following results (in wt.%): SiO_2
25 41.69, TiO_2 5.30, Al_2O_3 13.65, Cr_2O_3 0.09, Fe_2O_3 4.52, MgO 15.54, CaO 11.03, MnO 0.11, FeO
26 2.83, Na_2O 2.88, K_2O 0.96, H_2O 0.70, F 0.24, Cl 0.08, $\text{O}=(\text{F},\text{Cl})$ -0.12, sum 99.50. On the basis of
27 24 anions per formula unit, the formula is
28 $(\text{Na}_{0.816}\text{K}_{0.179})_{\Sigma=0.995}(\text{Ca}_{1.726}\text{Fe}^{2+}_{0.258}\text{Mn}_{0.014})_{\Sigma=1.998}(\text{Mg}_{3.383}\text{Fe}^{2+}_{0.088}\text{Ti}_{0.582}\text{Fe}^{3+}_{0.497}\text{Al}_{0.439}\text{Cr}_{0.011})_{\Sigma=5.00}(\text{Si}_{6.089}\text{Al}_{1.911})_{\Sigma=8.00}\text{O}_{22}[\text{O}_{1.187}(\text{OH})_{0.682}\text{F}_{0.111}\text{Cl}_{0.020}]_{\Sigma=2.00}$. Ferri-kaersutite is monoclinic with space group $C2/m$. Its
29 unit-cell parameters are $a = 9.8378(8)$, $b = 18.0562(9)$, $c = 5.3027(4)$ Å, $\beta = 105.199(9)^\circ$, $V = 908.99(13)$ Å³, $Z = 2$. The five strongest reflections in its X-ray powder diffraction pattern [d in Å
30 (relative visual intensity, hkl)] are: 2.707 (s, 151), 3.115 (ms, 310), 8.4 (s, 110), 3.379 (ms, 131),
31 2.598 (ms, 061). The crystal structure of ferri-kaersutite has been refined on the basis of 1783
32 observed reflections [$F_o > 4\sigma(F_o)$] with a final $R_1 = 0.038$.

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35 The relatively large equivalent isotropic displacement parameter at $M(1)$, with respect to those at
36 $M(2)$ and $M(3)$ sites, together with the short $M(1)$ – $\text{O}(3)$ distance, suggest the occurrence of Ti^{4+} at
37 the $M(1)$ site, whereas the small octahedral distortion at this site suggests a low Fe^{3+} occupancy.
38 This element is mainly hosted at the $M(2)$ and $M(3)$ sites.

39 The occurrence of amphiboles in the magma source region is notably relevant. The melting of Ti-
40 rich amphibole in the lithosphere and subsequent degrees of melt/host peridotite reactions are able
41 to produce melts which account for the compositional spectrum ranging from extreme alkaline lavas
42 to the most common alkaline basalts. In particular, when this amphibole is formed by reaction
43 between a peridotite matrix and metasomatic melts/fluids with high $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio, its subsequent
44 melting can influence primary volatile contents and ultimately magma rheology.

45
46 **Keywords:** ferri-kaersutite, new mineral, crystal-chemistry, oxo-amphibole, Victoria Land,
47 Antarctica.

INTRODUCTION

Among the 89 currently valid mineral species within the amphibole supergroup (<http://ima-cnmnc.nrm.se/imalist.htm> – IMA list of minerals), only six belong to the oxo-amphibole group (Table 1), i.e. amphiboles having $^W\text{O}^{2-} > ^W(\text{OH}+\text{F}+\text{Cl})^-$.

A mineralogical and petrological study of amphiboles occurring in mantle xenoliths from Harrow Peaks, Victoria Land, Antarctica revealed the presence of an amphibole approaching the end-member formula $\text{NaCa}_2(\text{Mg}_3\text{TiFe}^{3+})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$, i.e. ferri-kaersutite according to the new amphibole nomenclature (Hawthorne et al. 2012).

Previously a mineral belonging to the oxo-amphibole group was submitted to the IMA CNMNC and approved with the name ferrikaersutite (IMA 2011-035 – Zaitsev et al. 2011). Shortly thereafter, following the new IMA report on the nomenclature of the amphibole supergroup (Hawthorne et al. 2012), both the assigned name and the end-member formula were found to be wrong. Therefore, IMA 2011-035 was renamed oxo-magnesio-hastingsite, with ideal formula $\text{NaCa}_2(\text{Mg}_2\text{Fe}^{3+}_3)(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$ (Zaisev et al. 2013).

The aim of this paper is the description of the new mineral ferri-kaersutite from Harrow Peaks, Victoria Land, Antarctica. The mineral and its name have been approved by the IMA-CNMNC, under the number IMA 2014-051. The holotype material is deposited in the mineralogical collections of the Museo di Storia Naturale, University of Pisa, Via Roma 79, Calci, Pisa, Italy, under catalog number 19689.

OCCURRENCE

Ferri-kaersutite was identified in an ultramafic xenolith occurring in Cenozoic alkaline mafic lava from Harrow Peaks, Northern Victoria Land (NVL), Antarctica (latitude 74.02785°S, longitude 164.47466°E, 335 m above sea level – Fig. 1). The Cenozoic igneous activity in NVL was related to the West Antarctic Rift System and it was characterized by intrusions, dyke swarms, and volcanoes (Fitzgerald et al. 1987; Wörner 1999; Rocchi et al. 2002). Mantle xenoliths, brought to the surface by alkaline magmas, revealed upper mantle heterogeneities in this area, which result from combined effects of partial melting episodes and diffuse metasomatic enrichment (Zipfel and Wörner 1992; Coltorti et al. 2004; Perinelli et al. 2006; Melchiorre et al. 2011; Perinelli et al. 2012; Bonadiman et al. 2014). The occurrence of amphiboles in mantle parageneses is particularly intriguing because their crystal-chemistry is closely related to the chemical-physical conditions of the percolating fluids at upper mantle level.

Ferri-kaersutite was found in a spinel-bearing lherzolite having a 5 cm diameter. The sample shows a protogranular texture (Mercier and Nicolas 1975) and, accordingly, it does not show any

84 pronounced fabric orientation. The mineral assemblage does not provide any evidence of infiltration
85 of the host basalt or superficial alteration. Amphibole occurs as disseminated grains texturally
86 related to diopside and Cr-bearing spinel, as observed in the nearby xenoliths population from
87 Baker Rocks and Greene Point (Coltorti et al. 2004; Perinelli et al. 2012; Bonadiman et al. 2014).

88 89 **MINERAL DESCRIPTION**

90 Ferri-kaersutite occurs as brown euhedral prismatic crystals, up to 200 μm in length. It has a
91 vitreous luster. It is brittle, with a perfect $\{110\}$ cleavage. Owing to the very low amount of
92 available material (only two grains), some physical properties could not be measured, such as
93 streak, micro-hardness, density, and optical properties. Calculated density, based on the empirical
94 formula (see below) is 3.190 g/cm^3 , whereas the density corresponding to the end-member formula
95 is 3.237 g/cm^3 .

96 97 **CHEMICAL COMPOSITION**

98 Quantitative chemical analyses of ferri-kaersutite were carried out using a CAMECA SX-50
99 electron microprobe operating in wavelength-dispersive mode, with accelerating voltage 15 kV,
100 beam current 15 nA, and beam size 1 μm . The standards (element, emission line, counting times for
101 peak positions) are: diopside (Si $K\alpha$ 10 s, Ca $K\alpha$ 10 s), synthetic MnTiO_3 (Ti $K\alpha$ 10 s, Mn $K\alpha$ 10 s),
102 plagioclase (Na $K\alpha$ 10 s), orthoclase (K $K\alpha$ 7 s), periclase (Mg $K\alpha$ 10 s), corundum (Al $K\alpha$ 10 s),
103 hematite (Fe $K\alpha$ 10 s), and synthetic Cr_2O_3 (Cr $K\alpha$ 10 s). Raw counts were processed using the PAP
104 data reduction method (Pouchou and Pichoir 1985). The average of 10 spot analyses is given in
105 Table 2. No chemical zoning was observed in the studied crystal.

106 Secondary Ion Mass Spectroscopy (SIMS) measurements were performed with a CAMECA
107 IMS 4f ion microprobe. A 12.5 kV accelerated ^{16}O -primary ion beam was used with a current
108 intensity of 7-10 nA and ~ 10 -15 μm beam diameter. The mounts of both the sample and the
109 standards were left to degas overnight in the ion-microprobe sample chamber. Secondary ion
110 signals of the following isotopes were monitored at the electron multiplier: $^1\text{H}^+$, $^{19}\text{F}^+$, $^{37}\text{Cl}^+$ and $^{30}\text{Si}^+$
111 (the latter was used as the internal reference for the matrix). Acquisition times were 20 s (H), 50 s
112 (Cl), 50 s (F) and 15 s (Si) over five analytical cycles. Detection of positive secondary ions in the
113 range of 75-125 eV emission kinetic energies was obtained under steady-state sputtering conditions
114 after pre-sputtering. Mass calibration was checked before each analysis. Empirical corrections were
115 adopted for the "Ion Yields" IY(H/Si) to account for the variation of the ion signals with
116 increasing (Fe + Mn) content in the sample, as fully described by Ottolini et al. (2001, 2002). The
117 precision of the H determination was estimated on the basis of the reproducibility of the standard

118 analyses and was better than 8 % (Ottolini et al. 1993, 1995). The overall accuracy of the volatile
119 and light element determination at the concentration level exhibited by the samples of this work is
120 better than 15 %.

121 Finally, micro-Mössbauer spectroscopy was used for the determination of the Fe²⁺-Fe³⁺
122 ratio. A Mössbauer spectrum (Fig. 2) was collected in transmission mode at room temperature on a
123 constant acceleration Mössbauer spectrometer with a nominal 370 MBq ⁵⁷Co high specific activity
124 source in a 12 µm thick Rh matrix. The velocity scale was calibrated relative to 25 µm thick α-Fe
125 foil using the positions certified for (former) National Bureau of Standards standard reference
126 material no. 1541. Mössbauer spectra were fitted to three Lorentzian doublets and the usual
127 constraints were applied to all doublets (equal component areas and widths) using the program
128 MossA (Prescher et al. 2012). Area asymmetry due to preferred orientation was explored and the
129 value of Fe³⁺/Fe_{tot} was calculated based on relative area ratios, where uncertainties were estimated
130 based on fitting statistics. The preliminary Fe³⁺/Fe_{tot} estimate of 59(7) % was used for structure and
131 composition calculations, but this value was subsequently refined to 57(7) % from a spectrum with
132 a longer collection time (Fig. 2). We note that the two values of Fe³⁺/Fe_{tot} are indistinguishable
133 within experimental uncertainty and there is no observable influence of the difference in values on
134 any of the conclusions.

135 The chemical formula based on 24 anions (O, OH, F, Cl) was calculated using the value of
136 Fe³⁺/Fe_{tot} of 59(7) % measured by micro-Mössbauer and OH, F and Cl measured by SIMS (Table
137 2). All manganese was assumed as Mn²⁺, even if in other oxo-amphiboles (e.g., mangano-mangani-
138 ungarrettiite) manganese is known to partially occur as Mn³⁺. However, owing to its very low
139 content (0.01 atoms per formula unit, apfu), the oxidation state of manganese is not a crucial factor
140 for classification purposes.

141 The empirical formula of ferri-kaersutite is:
142 (Na_{0.816}K_{0.179})_{Σ=0.995}(Ca_{1.726}Fe²⁺_{0.258}Mn_{0.014})_{Σ=1.998}(Mg_{3.383}Fe²⁺_{0.088}Fe³⁺_{0.497}Al_{0.439}Cr_{0.011}Ti_{0.582})_{Σ=5.00}(Si
143 _{6.089}Al_{1.911})_{Σ=8.00}O₂₂[O_{1.187}(OH)_{0.682}F_{0.111}Cl_{0.020}]_{Σ=2.00}. The ideal formula is
144 NaCa₂(Mg₃Fe³⁺Ti)(Si₆Al₂)O₂₂O₂, which requires SiO₂ 40.68, Fe₂O₃ 9.01, MgO 13.64, TiO₂ 9.01,
145 CaO 12.65, Na₂O 3.50, total 100.00 wt.%.

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147 X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

148 A quasi-powder X-ray diffraction pattern of ferri-kaersutite was obtained using a 114.6 mm
149 diameter Gandolfi camera and Ni-filtered Cu Kα radiation. The observed X-ray powder pattern is
150 compared in Table 3 with that calculated using the software Powder Cell (Kraus and Nolze 1996).

151 Unit-cell parameters, refined using UnitCell (Holland and Redfern 1997), are $a = 9.845(11)$, $b =$
152 $18.064(10)$, $c = 5.312(6)$ Å, $\beta = 105.26(10)^\circ$, $V = 911.3(2)$ Å³.

153 Single-crystal X-ray diffraction data were collected using an Xcalibur diffractometer
154 equipped with a CCD area detector. Graphite-monochromatized MoK α radiation was used. Data
155 reduction was performed by using the package of software XcrysAlis (Agilent Technologies) and
156 an empirical absorption correction was applied by the ABSPACK software as implement in
157 XcrysAlis (Agilent Technologies). A statistical test ($|E^2-1| = 1.151$) and systematic absences
158 unequivocally confirmed the space group $C2/m$. Refined unit-cell parameters are $a = 9.8378(8)$, $b =$
159 $18.0562(9)$, $c = 5.3027(4)$ Å, $\beta = 105.199(9)^\circ$, $V = 908.99(13)$ Å³. The $a:b:c$ ratio, calculated from
160 single-crystal data, is 0.545:1:0.294.

161 The crystal structure of ferri-kaersutite was refined using Shelxl-97 (Sheldrick 2008) starting
162 from the atomic coordinates of kaersutite (Comodi et al. 2010). Scattering curves for neutral atoms
163 were taken from the *International Tables for Crystallography* (Wilson 1992). The occupancies of
164 the cation sites were refined using the following scattering curves: $M(1)$, $M(2)$, $M(3)$ sites: Mg vs.
165 Fe; $M(4)$ site: Ca vs. □; $M(4')$: Fe vs. □; A sites: Na vs. □; $T(1)$, $T(2)$ sites: Si vs. □. $T(1)$ and $T(2)$
166 were found fully-occupied by Si and their site occupancies were then fixed on the basis of chemical
167 data, calculating the ^{T(1)}Al content on the basis of the relationship proposed by Oberti et al. (2007).
168 The correct positions of the $M(4')$ and the split A sites, i.e. $A(m)$ and $A(2)$, were found by
169 difference-Fourier maps. After several cycles of isotropic refinement, the R_1 value converged to
170 0.083. By introducing anisotropic displacement parameters for the cation sites, the refinement
171 converged to $R_1 = 0.047$. Finally, anisotropic displacement parameters of anions were introduced.
172 The refinement converged to the final R_1 value of 0.038. In the difference-Fourier maps, the highest
173 maximum is at 0.67 Å from O(3), possibly related to the occurrence of a partially occupied H
174 position at coordinates (0.18, 0, 0.73). These atom coordinates are similar to those expected for the
175 H atom, even if the corresponding H–O distance is too short. Details of the crystal structure
176 refinement are given in Table 4, whereas atomic coordinates and anisotropic displacement
177 parameters are shown in Table 5. Table 6 gives selected bond distances for cation sites.

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179

CRYSTAL-CHEMISTRY OF FERRI-KAERSUTITE

180 The crystal structure of ferri-kaersutite agrees with the general features of the monoclinic
181 $C2/m$ amphiboles, which are formed by a double chain of corner-sharing $T(1)$ and $T(2)$ tetrahedra
182 and a strip of edge-sharing $M(1)$, $M(2)$, and $M(3)$ octahedra, extending in the c direction. The $M(4)$
183 site occurs at the junction between the strip of octahedra and the double chain of tetrahedra,
184 whereas the A site is located in a large cavity at the centre of the hexagonal ring of tetrahedra

185 (Hawthorne and Oberti 2007). The site population of our specimen of ferri-kaersutite was derived
186 by comparing the refined site-scattering values and the unit formula calculated from chemical
187 analyses (Table 7), in agreement with Hawthorne et al. (1995b). Bond-valence balance, calculated
188 following the values given by Brese and O’Keeffe (1991), is reported in Table 8.

189 **The *T* sites**

190 The two independent *T*(1) and *T*(2) sites have average bond distances of 1.672 and 1.638
191 Å, respectively. The average bond distance for *T*(1) is larger than that for the *T*(2) site, in agreement
192 with the strong tendency of Al to be partitioned at the *T*(1) site in *C2/m* amphiboles. Oberti et al.
193 (2007) proposed a linear relation between $\langle T(1)-O \rangle$ and $T(1)Al$, namely $T(1)Al (apfu) = [\langle T(1)-O \rangle -$
194 $1.6193] \times 34.2199$. By applying this equation, the calculated $T(1)Al$ content is 1.803 *apfu*.
195 Consequently, the proposed site occupancies at the *T*(1) and *T*(2) sites are (Si_{2.197}Al_{1.803}) and
196 (Si_{3.892}Al_{0.108}), respectively. These site occupancies agree with the bond valence requirements
197 (Table 8). The site-scattering associated with the *T* sites does not indicate any presence of Ti at
198 these sites.

199 **The *M*(1), *M*(2), *M*(3) sites**

200 The total refined site-scattering at the *M*(1), *M*(2), and *M*(3) sites is 75.6 electrons per
201 formula unit (*epfu*); the total calculated site-scattering of C cations in the formula unit of ferri-
202 kaersutite is 74.6 *epfu* (Table 7), which is sufficiently close to allow us to derive a site population
203 from the data of Table 2 and Table 7.

204 The average bond distances are 2.067, 2.063, and 2.071 Å for *M*(1), *M*(2), and *M*(3) sites,
205 respectively. Examination of the *M*–*M* distances (Table 6) shows that the *M*(1)–*M*(1) interatomic
206 distance is shorter than the other *M*–*M* distances, indicating that *M*(1) cations are displaced toward
207 the O(3)–O(3) edge, as observed in amphiboles containing significant O²⁻ at the O(3) site and high-
208 charge cations at the *M*(1) site (e.g., mangani-mangano-ungarettiite, Hawthorne et al. 1995a;
209 mangani-obertiite, Hawthorne et al. 2000; mangani-dellaventuraitite, Tait et al. 2005; oxo-magnesio-
210 hastingsite, Zaitsev et al. 2013). In addition, following Oberti et al. (2007), the *M*(1)–*M*(2)
211 interatomic distance is sensitive to the presence of an oxo-component at the O(3) site. By using the
212 regression equation derived by Oberti et al. (2007) for pargasite-kaersutite-hastingsite, an O⁽³⁾O²⁻
213 content of 1.26 *apfu* can be calculated, in good agreement with 1.19 O⁽³⁾O²⁻ obtained from chemical
214 analyses. For this reason, all Ti⁴⁺ was assigned to the *M*(1) site, providing local electroneutrality to
215 the oxo-component at the O(3) site through the substitution $M(1)Ti^{4+} + 2O(3)O^{2-} = M(1)(Mg,Fe)^{2+} +$
216 $2O(3)OH$. The assignment of this element at the *M*(1) site agrees with the relatively larger U_{eq} value
217 compared to those of the other *M* sites (Tiepolo et al. 1999), because Ti does not occupy the same
218 position as Mg, Fe²⁺, and Fe³⁺, owing to its typical off-center displacement (e.g., Megaw 1968). The

219 anisotropic displacement ellipsoid of the $M(1)$ site is elongated parallel to [010] (see Table 5). In
220 some cases, the splitting of this site has been reported (e.g., Hawthorne et al. 2000). The low value
221 of the octahedral distortion of the $M(1)$ site, as defined by Brown and Shannon (1973), suggests a
222 low occupancy by Fe^{3+} at this site, in agreement with Oberti et al. (2007). Consequently, a mixed
223 ($\text{Mg}, \text{Ti}, \text{Fe}^{3+}$) site occupancy can be proposed at the $M(1)$ site. The calculated bond distance is 2.053
224 Å, compared with the observed value of 2.067 Å.

225 Hawthorne and Oberti (2007) illustrate the well-developed linear correlation between
226 $\langle M(2)\text{-O} \rangle$ and the aggregate size of the constituent cations. By using their relations, an aggregate
227 size of ≈ 0.69 Å can be obtained, compared with a calculated aggregate size of 0.67 Å resulting from
228 the $M(2)$ site population reported in Table 7 and the ionic radii given by Shannon (1976).
229 Consequently, $M(2)$ could be a mixed ($\text{Mg}, \text{Al}, \text{Fe}^{3+}, \text{Cr}$) site. The calculated bond length, 2.046 Å, is
230 shorter than the observed value, 2.063 Å. It is interesting to note that aluminum is disordered
231 between the $M(2)$ and $M(3)$ sites, as reported in other mantle amphiboles (e.g., Oberti et al. 1995).
232 Analogously, Cr^{3+} could be disordered over $M(2)$ and $M(3)$ sites, but its very low content does not
233 allow a more accurate determination of the partitioning of this element between the two octahedral
234 sites.

235 The $M(3)$ site hosts Mg , Fe^{3+} , Al , and Fe^{2+} . The latter cation was assigned to this position,
236 owing to its preferential partitioning at the $M(3)$ site with respect to $M(1)$ and, in particular, to $M(2)$
237 (Oberti et al. 2007). Its calculated average bond distance is 2.050 Å, which is shorter than the
238 observed $\langle M(3)\text{-O} \rangle$ value, 2.071 Å.

239 **The $M(4)$ site**

240 In ferri-kaersutite, $M(4)$ is split into two sub-positions, $M(4)$ and $M(4')$; this splitting has
241 been reported by other authors studying amphiboles having a significant amount of $^{\text{B}}(\text{Mg}, \text{Fe}, \text{Mn})$,
242 e.g., Oberti and Ghose (1993).

243 $M(4)$ hosts Ca , whereas $M(4')$ is occupied by Fe^{2+} and Mn^{2+} . The coordination of the latter
244 position is characterized by four short distances, ranging from 2.030 to 2.266 Å, and four longer
245 ones (at 2.95 and 2.97 Å). On the contrary, according to Oberti et al. (2007), the coordination of this
246 split sub-positions should be six-fold. In our opinion, this discrepancy may be related to the low
247 accuracy in the determination of the $M(4')$ position, owing to its low site occupancy.

248 **The A site**

249 As reported by Hawthorne and Oberti (2007), the A cations do not occupy the central site
250 $A(2/m)$ but are split into two sub-positions, $A(m)$ and $A(2)$. The former is confined to the mirror
251 plane, whereas the latter is displaced along the [010] direction. The average bond distances of the
252 two sub-positions are 2.731 and 2.622 Å for $A(m)$ and $A(2)$, respectively, suggesting a preferential

253 occupancy of K at the $A(m)$ site, in agreement with Hawthorne and Oberti (2007). Notwithstanding
254 the difficulty in giving reliable site populations for the split A sites, we could hypothesize a mixed
255 (Na,K) site population at the $A(m)$ position, whereas $A(2)$ could be partially occupied by Na only.

256

257 GENETIC CONDITIONS OF FERRI-KAERSUTITE

258 The full characterization of the crystal-chemistry of amphiboles provides an useful tool for
259 unraveling their crystallization conditions. Indeed, the partitioning of Al between $T(1)$ and $T(2)$ sites
260 as well as the (Mg,Fe) content at the $M(4')$ position are related to the crystallization temperature
261 (Oberti et al. 2007).

262 The ^{IV}Al partitioning at $T(2)$ site, before reaching 2.0 apfu at the $T(1)$ site, is a signal of HT
263 conditions of crystallization, while complete Al ordering at $T(1)$ suggests temperatures lower than
264 $850^{\circ}C$ (e.g., Perinelli et al. 2012). Ferri-kaersutite agrees with the preferential partitioning of Al at
265 the $T(1)$ site; indeed this site has an Al/(Al+Si) atomic ratio close to 0.45, suggesting a
266 crystallization temperature of $850 \pm 50^{\circ}C$. In addition, as stated above, the $M(4')$ site, hosting Mg
267 and Fe^{2+} , is also sensitive to temperature (Oberti et al. 2007). In particular, the ordering of Fe^{2+} at
268 $M(4')$ increases with increasing temperature. This direct correlation, first shown by Oberti et al.
269 (2007), fits well for ferri-kaersutite that contains up to 0.258 a.p.f.u. of $^{M(4')}Fe^{2+}$, suggesting a
270 relatively high crystallization temperature ($\sim 850^{\circ}C$), consistent with Al partitioning at the
271 tetrahedral sites.

272 All of these observations are in good agreement with world-wide amphiboles from mantle
273 environments (Oberti et al. 2007), although the chemical composition of ferri-kaersutite indicates
274 uncommonly high oxidizing conditions as well as a low Al content in the bulk system. The
275 temperatures obtained by these unconventional geothermometers based on crystallographic
276 constraints are in agreement with the independent temperature estimate of $845 \pm 30^{\circ}C$ (for $n = 8$)
277 calculated at a constant pressure of 1.5 GPa using the opx-cpx geothermometer proposed by Brey
278 and Köler (1990) (BKN90). The pressure was chosen taking into account the spinel stability and the
279 mantle silicate parageneses.

280

281 IMPLICATIONS

282 There is a general consensus (e.g. Niu 2008; Pilet et al. 2008) that Ti-rich amphibole (Ti-
283 rich pargasite and kaersutite) plays an important role in the genesis of alkaline magma. In the upper
284 mantle, Ti-rich amphibole commonly occurs as disseminated crystals or veinlets in a peridotite
285 matrix (i.e., Coltorti et al. 2004; Tiepolo et al. 2011) or as large discrete veins structurally isolated
286 by the peridotite matrix (Gregoire et al. 2000). The discovery of a ferric component in the Ti-rich

287 kaersutite group in the upper mantle provides new information about metasomatic redox processes
288 acting in the mantle. The formation of ferri-kaersutite suggests that the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of the
289 metasomatic silicate melts was high, and/or that the volatile rich melt/fluid percolated through and
290 reacted with the peridotite, concentrating Fe^{3+} and C-O-H volatile species, and increasing $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$
291 until the crystallization of ferri-karsutite. The melting of Ti-rich amphibole veins in the lithosphere
292 and subsequent degrees of melt/host peridotite reactions produce melts which can account for the
293 wide compositional spectrum in magmatic products, i.e. from extreme alkaline lavas (i.e.
294 nephelinite, basanite) to the most common alkaline basalts (Fitton and Upton 1987; Pilet et al.
295 2008). The analyses of volatile contents and the Fe speciation in Ti-rich mantle amphibole is,
296 therefore, crucial to the characterization of the upper mantle redox conditions and volatile
297 circulation, and ultimately sheds light on one of the most intriguing aspects of magma genesis, the
298 volatile contents of the primary magma.

299
300

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438 **Table captions**

439 **Table 1.** Valid species belonging to the oxo-amphibole group.

440 **Table 2.** Chemical composition of ferri-kaersutite (as wt.% - average of 10 spot analyses) and
441 number of atoms per formula unit (apfu) based on 24 anions per formula unit. FeO_{tot} (wt.%) from
442 microprobe analysis; (***) Fe₂O₃ and FeO (wt.%) from Mössbauer spectroscopy.

443 **Table 3.** X-ray powder diffraction data for ferri-kaersutite.

444 **Table 4.** Crystal data and summary of parameters describing data collection and refinement for
445 ferri-kaersutite.

446 **Table 5.** Atomic positions and displacement parameters (in Å²) for ferri-kaersutite.

447 **Table 6.** Selected interatomic distances (in Å) and angles (in °) for ferri-kaersutite.

448 **Table 7.** Refined site scattering values (in electrons per formula unit, epfu) and assigned site
449 populations (in atoms per formula unit, apfu).

450 **Table 8.** Bond valence sums according to bond-valence parameters taken from Brese and O’Keeffe
451 (1991).

452

453 **Figure captions**

454 **Fig. 1.** Location map of Northern Victoria Land (after Giacomoni et al. 2013).

455 **Fig. 2.** Room temperature Mössbauer spectrum of ferri-kaersutite. The doublets assigned to Fe²⁺
456 and Fe³⁺ are shaded grey and black, respectively.

457

Table 1. Valid oxo-amphiboles.

Mineral species	Chemical formula	Ref.
Ferro-ferri-obertiite	$\text{NaNa}_2(\text{Fe}^{2+}_3\text{TiFe}^{3+})\text{Si}_8\text{O}_{22}\text{O}_2$	[1]
Kaersutite	$\text{NaCa}_2(\text{Mg}_3\text{TiAl})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$	[2]
Mangani-dellaventuraite	$\text{NaNa}_2(\text{MgMn}^{3+}_2\text{TiLi})\text{Si}_8\text{O}_{22}\text{O}_2$	[3]
Mangani-obertiite	$\text{NaNa}_2(\text{Mg}_3\text{TiMn}^{3+})\text{Si}_8\text{O}_{22}\text{O}_2$	[4]
Mangano-mangani-ungarettiite	$\text{NaNa}_2(\text{Mn}^{2+}_2\text{Mn}^{3+}_3)\text{Si}_8\text{O}_{22}\text{O}_2$	[5]
Oxo-magnesio-hastingsite	$\text{NaCa}_2(\text{Mg}_2\text{Fe}^{3+}_3)(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}_2$	[6]

[1] Hawthorne et al. 2010; [2] Comodi et al. 2010; [3] Tait et al. 2005; [4] Hawthorne et al. 2000;
[5] Hawthorne et al. 1995a; [6] Zaitsev et al. 2013.

Table 2. Chemical composition of ferri-kaersutite (as wt.% - average of 10 spot analyses) and number of atoms per formula unit (apfu) based on 24 anions per formula unit. FeO_{tot} (wt.%) from microprobe analysis; (**) Fe₂O₃ and FeO (wt.%) from Mössbauer spectroscopy; F (wt.%), Cl (wt.%) and H₂O (wt.%) from SIMS.

oxide	wt%	range	e.s.d.	Element	apfu	range	e.s.d.
SiO ₂	41.69	41.29-41.90	0.29	Si ⁴⁺	6.089	6.053-6.125	0.024
TiO ₂	5.30	5.23-5.44	0.09	Ti ⁴⁺	0.582	0.570-0.600	0.012
Al ₂ O ₃	13.65	13.23-14.01	0.32	Al ³⁺	2.350	2.276-2.416	0.057
Cr ₂ O ₃	0.09	0.08-0.12	0.02	Cr ³⁺	0.011	0.009-0.014	0.002
Fe ₂ O ₃	4.52			Fe ³⁺	0.497	0.464-0.524	0.023
FeO	2.83			Fe ²⁺	0.346	0.322-0.364	0.016
FeO _{tot}	6.90	6.47-7.25	0.33				
MnO	0.11	0.08-0.13	0.02	Mn ²⁺	0.014	0.010-0.017	0.003
MgO	15.54	15.29-15.70	0.18	Mg ²⁺	3.383	3.331-3.445	0.042
CaO	11.03	10.94-11.20	0.12	Ca ²⁺	1.726	1.712-1.746	0.014
Na ₂ O	2.88	2.80-2.99	0.08	Na ⁺	0.816	0.788-0.847	0.022
K ₂ O	0.96	0.94-0.98	0.02	K ⁺	0.179	0.175-0.184	0.003
H ₂ O	0.70	0.65-0.72	0.03	OH ⁻	0.682	0.678-0.687	0.003
F	0.24	0.23-0.27	0.02	F ⁻	0.111	0.110-0.112	0.000
Cl	0.08	0.07-0.08	0.01	Cl ⁻	0.020	0.020-0.020	0.000
Total	99.62	99.00-100.22	0.35	O ²⁻	23.187	23.181 – 23.192	0.004
O = F,Cl	-0.12						
Sum	99.50	98.88 – 100.10	0.35				

Table 3. X-ray powder diffraction data for ferri-kaersutite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl	
-	-	18	9.03	0 2 0	
s	8.4	70	8.40	1 1 0	*
vw	4.85	16	4.91	-1 1 1	
vw	4.52	18	4.51	0 4 0	*
vw	4.229				
-	-	14	3.890	-1 3 1	
vw	3.703				
ms	3.379	67	3.377	1 3 1	*
m	3.266	47	3.271	2 4 0	*
ms	3.115	78	3.117	3 1 0	*
vw	3.035	4	3.033	-3 1 1	*
m	2.938	42	2.931	2 2 1	*
vw	2.867				
vw	2.806	13	2.801	3 3 0	*
w	2.739	33	2.739	-3 3 1	*
s	2.707	100	2.704	1 5 1	*
ms	2.598	61	2.594	0 6 1	*
-	-	72	2.549	-2 0 2	
mw	2.344	42	2.342	-3 5 1	*
w	2.336	18	2.326	-4 2 1	
w	2.305	15	2.302	-1 7 1	*
		18	2.289	-3 1 2	
vw	2.221	8	2.219	-2 4 2	*
mw	2.158	38	2.159	2 6 1	*
mw	2.041	21	2.040	2 0 2	*
vw	2.030	16	2.025	-4 0 2	*
vw	2.014	17	2.012	3 5 1	*
vw	1.868	12	1.867	-1 9 1	*
w	1.648	29	1.646	4 6 1	*

Notes: the d_{hkl} values were calculated on the basis of the unit cell refined by using single-crystal data. Intensities were calculated on the basis of the structural model using the software Powder Cell (Kraus and Nolze 1996). Observed intensities were visually estimated. vs = very strong; s = strong; ms = medium-strong; m = medium; mw = medium-weak; w = weak; vw = very weak. Only reflections with $I_{\text{calc}} > 5$ are listed, if not observed. The seven strongest reflections are given in bold. Reflections used for the refinement of the unit-cell parameters are indicated by an asterisk.

Table 4. Crystal data and summary of parameters describing data collection and refinement for ferri-kaersutite.

Crystal data	
Crystal size (mm ³)	0.20 x 0.17 x 0.10
Cell setting, space group	Monoclinic, <i>C2/m</i>
<i>a</i> (Å)	9.8378(8)
<i>b</i> (Å)	18.0562(9)
<i>c</i> (Å)	5.3027(6)
β (°)	105.199(9)
<i>V</i> (Å ³)	908.99(13)
<i>Z</i>	2
Data collection and refinement	
Radiation, wavelength (Å)	Mo <i>K</i> α , $\lambda = 0.71073$
Temperature (K)	293
$2\theta_{\max}$ (°)	70.28
Measured reflections	10645
Unique reflections	1924
Data completeness	0.956
Reflections with $F_o > 4\sigma(F_o)$	1783
R_{int}	0.0289
$R\sigma$	0.0142
Range of indices	$-15 \leq h \leq 15,$ $-29 \leq k \leq 29,$ $-8 \leq l \leq 8$
$R [F_o > 4\sigma(F_o)]$	0.0385
R (all data)	0.0408
wR (on F_o^2)	0.1125
Goof	1.110
Number of least-squares parameters	111
Maximum peak in the difference Fourier synthesis ($e \text{ \AA}^{-3}$)	0.76 [at 0.67 Å from O(3)]
Maximum hole in the difference Fourier synthesis ($e \text{ \AA}^{-3}$)	-1.13 [at 0.53 Å from M(4)]
<i>Note:</i> the weighting scheme is defined as $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$. <i>a</i> and <i>b</i> values are 0.0600 and 2.6761.	

Table 5. Atomic positions and displacement parameters (\AA^2) for ferri-kaersutite.

Site	x/a	y/b	z/c	U_{33}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
<i>T</i> (1)	0.28309(5)	0.08524(3)	0.30190(10)	0.0080(1)	0.0077(2)	0.0090(2)	0.0074(2)	-0.0004(1)	0.0024(2)	-0.0009(1)
<i>T</i> (2)	0.29117(5)	0.17265(2)	0.80969(9)	0.0082(1)	0.0077(2)	0.0090(2)	0.0074(2)	0.0004(1)	0.0026(2)	-0.0009(1)
<i>M</i> (1)	0	0.08338(4)	½	0.0131(2)	0.0082(3)	0.0261(4)	0.0062(4)	0	0.0038(2)	0
<i>M</i> (2)	0	0.17695(3)	0	0.0074(2)	0.0074(3)	0.0086(3)	0.0066(4)	0	0.0028(2)	0
<i>M</i> (3)	0	0	0	0.0097(3)	0.0106(4)	0.0099(4)	0.0083(5)	0	0.0021(3)	0
<i>M</i> (4)	0	0.27805(5)	½	0.0145(2)	0.0155(2)	0.0159(4)	0.0148(3)	0	0.0088(2)	0
<i>M</i> (4 [*])	0	0.2502(12)	½	0.0145(2)	0.0155(2)	0.0159(4)	0.0148(3)	0	0.0088(2)	0
<i>A</i> (<i>m</i>)	0.0425(7)	½	0.0838(15)	0.058(2)	0.097(4)	0.022(2)	0.089(4)	0	0.087(3)	0
<i>A</i> (2)	0	0.473(10)	0	0.058(2)	0.097(4)	0.022(2)	0.089(4)	0	0.087(3)	0
<i>O</i> (1)	0.1078(1)	0.08679(7)	0.2192(3)	0.0113(2)	0.0092(5)	0.0140(5)	0.0107(6)	-0.0006(4)	0.0031(4)	-0.0014(4)
<i>O</i> (2)	0.1189(1)	0.17159(7)	0.7278(3)	0.0109(2)	0.0078(4)	0.0142(5)	0.0107(6)	0.0008(4)	0.0025(4)	-0.0003(4)
<i>O</i> (3)	0.1078(2)	0	0.7126(4)	0.0145(3)	0.0117(7)	0.0181(8)	0.0139(9)	0	0.0033(6)	0
<i>O</i> (4)	0.3656(1)	0.25065(7)	0.7878(3)	0.0144(2)	0.0157(5)	0.0127(5)	0.0152(6)	0.0008(4)	0.0047(5)	-0.0039(4)
<i>O</i> (5)	0.3505(1)	0.13952(8)	0.1074(3)	0.0147(3)	0.0113(5)	0.0195(6)	0.0124(6)	0.0061(4)	0.0017(4)	-0.0001(4)
<i>O</i> (6)	0.3469(1)	0.11743(8)	0.6066(3)	0.0153(3)	0.0119(5)	0.0196(6)	0.0147(6)	-0.0058(4)	0.0041(5)	0.0008(4)
<i>O</i> (7)	0.3438(2)	0	0.2802(4)	0.0178(4)	0.0146(8)	0.0154(8)	0.0231(10)	0	0.0044(7)	0

Table 6. Selected interatomic distances (Å) and angles (°) for ferri-kaersutite.

<i>T</i> (1)	-O(1)	1.665(1)	<i>T</i> (2)	-O(4)	1.606(1)	<i>M</i> (1)	-O(3)	2.009(1) × 2
	-O(7)	1.666(1)		-O(2)	1.636(1)		-O(1)	2.043(1) × 2
	-O(6)	1.677(1)		-O(5)	1.645(1)		-O(2)	2.150(1) × 2
	-O(5)	1.680(1)		-O(6)	1.662(1)		average	2.067
	average	1.672		average	1.637			
<i>M</i> (2)	-O(4)	1.986(1) × 2	<i>M</i> (3)	-O(1)	2.070(1) × 4	<i>M</i> (4)	-O(4)	2.325(1) × 2
	-O(2)	2.085(1) × 2		-O(3)	2.072(2) × 2		-O(2)	2.405(2) × 2
	-O(1)	2.116(1) × 2		average	2.071		-O(6)	2.568(2) × 2
	average	2.063					-O(5)	2.666(2) × 2
							average	2.491
<i>M</i> (4')	-O(2)	2.03(2) × 2	<i>A</i> (<i>m</i>)	-O(7)	2.444(5)	<i>A</i> (2)	-O(7)	2.452(4) × 2
	-O(4)	2.266(1) × 2		-O(7)	2.472(5)		-O(5)	2.652(14) × 2
	average			-O(6)	2.728(6) × 2		-O(6)	2.761(11) × 2
				-O(5)	3.007(3) × 2		average	2.622
				average	2.731			
<i>M</i> (1)– <i>M</i> (1)		3.011(2)	<i>M</i> (1)– <i>M</i> (4')		3.01(2)	<i>T</i> (1)–O(5)– <i>T</i> (2)		134.67(9)
<i>M</i> (1)– <i>M</i> (2)		3.1439(6)	<i>M</i> (2)– <i>M</i> (3)		3.1950(6)	<i>T</i> (1)–O(6)– <i>T</i> (2)		136.78(9)
<i>M</i> (1)– <i>M</i> (3)		3.0490(5)	<i>M</i> (2)– <i>M</i> (4)		3.2190(7)	<i>T</i> (1)–O(7)– <i>T</i> (1)		135.04(13)

Table 7. Refined site scattering values (in electrons per formula unit, epfu) and assigned site populations (in atoms per formula unit, apfu).

Site	Refined site-scattering (epfu)	Site-population (apfu)	Calculated site-scattering (epfu)
<i>M</i> (1)	31.6	Mg _{1.298} Ti _{0.582} Fe ³⁺ _{0.120}	31.5
<i>M</i> (2)	28.5	Mg _{1.389} Al _{0.339} Fe ³⁺ _{0.261} Cr _{0.011}	28.1
<i>M</i> (3)	15.5	Mg _{0.696} Fe ³⁺ _{0.116} Al _{0.100} Fe ²⁺ _{0.088}	15.0
<i>M</i> (4) + <i>M</i> (4')	40.4	Ca _{1.726} Fe ²⁺ _{0.258} Mn _{0.014}	41.6
<i>A</i> (<i>m</i>) + <i>A</i> (2)	12.5	Na _{0.816} K _{0.179}	12.4

Table 8. Bond valence sums according to bond-valence parameters taken from Brese and O’Keeffe (1991).

Site	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	Σ cations	Theor.
<i>T</i> (1)	0.93				0.89	0.90	0.92 _{↓x2}	3.64	3.55
<i>T</i> (2)		0.97		1.05	0.95	0.90		3.87	3.97
<i>M</i> (1)	0.44 ^{→x2}	0.33 ^{→x2}	0.49 ^{→x2} _{↓x2}					2.52	2.64
<i>M</i> (2)	0.32 ^{→x2}	0.35 ^{→x2}		0.46 ^{→x2}				2.26	2.31
<i>M</i> (3)	0.37 ^{→x4}		0.37 ^{→x2}					2.22	2.22
<i>M</i> (4) + <i>M</i> (4')		0.31 ^{→x2}		0.36 ^{→x2}	0.14 ^{→x2}	0.18 ^{→x2}		1.98	2.00
<i>A</i> (<i>m</i>) + <i>A</i> (2)					0.07 ^{→x2}	0.10 ^{→x2}	0.17 0.16 0.05 ^{→x2}	0.77	1.00
Σ anions	2.06	1.96	1.35	1.87	2.05	2.08	2.22		
Theor.	2.00	2.00	1.60	2.00	2.00	2.00	2.00		

Note: in mixed sites, bond-valence contribution of each cation has been weighted according to its occupancy.



