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2   Kangite, (Sc,Ti,Al,Zr,Mg,Ca,□)$_2$O$_3$, a new ultrarefractory scandia mineral

3   from the Allende meteorite: Synchrotron micro-Laue diffraction and

4   electron backscatter diffraction

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13   **ABSTRACT**

14   Kangite (IMA 2011-092), (Sc,Ti,Al,Zr,Mg,Ca,□)$_2$O$_3$, is a new scandia

15   mineral, occurring as micrometer-sized crystals with REE-rich perovskite and

16   spinel in a davisite-dominant ultrarefractory inclusion from the Allende CV3

17   carbonaceous chondrite. The phase was characterized by SEM, EBSD,

18   synchrotron micro-Laue diffraction, micro-Raman and EPMA. The mean

19   chemical composition of the type kangite is (wt%) TiO$_2$ 36.6, Sc$_2$O$_3$ 26.4, ZrO$_2$

20   11.3, Al$_2$O$_3$ 7.0, Y$_2$O$_3$ 5.4, CaO 3.9, MgO 3.14, Dy$_2$O$_3$ 1.8, SiO$_2$ 1.7, V$_2$O$_3$ 1.31,

21   Er$_2$O$_3$ 0.92, FeO 0.8, Gd$_2$O$_3$ 0.60, Ho$_2$O$_3$ 0.40, Tb$_2$O$_3$ 0.18, Cr$_2$O$_3$ 0.09, ThO$_2$

22   0.04, O -0.3, sum 101.28 with a corrected empirical formula calculated on the

23   basis of 3 O atoms of

24     $[(Sc_{0.54}Al_{0.16}Y_{0.07}V_{0.03}Gd_{0.01}Dy_{0.01}Er_{0.01})^{3+}_{\Sigma0.83}(Ti_{0.66}Zr_{0.13})^{4+}_{\Sigma0.79}(Mg_{0.11}Ca_{0.06}$

25     $Fe_{0.02})^{2+}_{\Sigma0.19}\square_{0.19}]_{\Sigma2.00}O_3$. Synchrotron micro-Laue diffraction (i.e., an energy

26   scan by a high flux X-ray monochromatic beam) on one type domain at

27   submicrometer resolution revealed that kangite has a cation deficient $Ia\overline{3}$

28   bixbyite-type cubic structure. The cell parameters are a = 9.842(1) Å, V =

29   953.3(1) Å^3, Z = 16, which leads to a calculated density of 3.879 g/cm^3. Kangite

30   is a new ultrarefractory mineral, likely originating through low temperature

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31   oxidation of a Sc-, Ti^{3+}-enriched high temperature condensate oxide dating to the

32   birth of the solar system.

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34   **Keywords**: Kangite, $(Sc,Ti,Al,Zr,Mg,Ca,\square)_2O_3$, new ultrarefractory mineral, scandia,

35   Allende meteorite, CV3 carbonaceous chondrite, synchrotron micro-Laue diffraction, EBSD.

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38   **INTRODUCTION**

39   During a nanomineralogy investigation of a previously described inclusion, ACM-3,

40   in the Allende meteorite (Ma and Rossman 2009b), a new ultrarefractory Sc-, Ti-rich mineral

41   $(Sc,Ti,Al,Zr,Mg,Ca,\square)_2O_3$, named "kangite," was discovered. Electron probe microanalysis

42   (EPMA), high-resolution scanning electron microscope (SEM), electron backscatter

43   diffraction (EBSD), synchrotron micro-Laue diffraction with subsequent energy scans, and

44   microRaman analyses were used to determine its composition, physical properties, and

45   structure and to characterize associated phases. Synthetic Sc_2O_3 is well-known but synthetic

46   $(Sc,Ti,Al,Zr,Mg,Ca,\square)_2O_3$ is unknown. Kangite is a new mineral species and a phase new to

47   meteoritics. In this paper, we describe the first occurrence of kangite in nature, as a new

48   ultrarefractory oxide, among the oldest solid materials in the solar system.

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50   **MINERAL NAME AND TYPE MATERIAL**

51   The mineral and the mineral name (kangite) have been approved by the Commission

52   on New Minerals, Nomenclature and Classification (CNMNC) of the International

53   Mineralogical Association (IMA 2011-092). The name is derived from "kang", the Chinese

54   word for the element scandium. Holotype material has been deposited under catalog USNM

55   7555 in the Smithsonian Institution's National Museum of Natural History, Washington DC,

56   USA. Section USNM 7555 also contains type davisite (IMA 2008-030; Ma and Rossman

57   2009b).

58

59   **OCCURRENCE**

60   The Allende meteorite fell in and near Pueblito de Allende, Chihuahua, Mexico on

61   February 8, 1969 (Clarke et al. 1971). This CV3 carbonaceous chondrite is probably the most

62   highly studied meteorite and the results of these studies have greatly influenced current

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63 thinking about processes, timing, and chemistry in the primitive solar nebula and in small

64 planetary bodies. The mineral kangite was found within one irregular ultrarefractory

65 inclusion, ACM-3, in one polished section (USNM 7555), prepared from a ~1 cm diameter

66 Allende fragment (Caltech Meteorite Collection No. Allende12A). ACM-3 is about 130 μm

67 in diameter in the section plane and is surrounded by a matrix of mostly fine-grained olivine

68 and troilite. Kangite occurs interstitially, along with perovskite and spinel, within an

69 aggregate of the type davisite crystals (Figs. 1-2). All four kangite grains are in contact with

70 davisite and two are also in contact with perovskite. One was observed in contact with

71 spinel.

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APPEARANCE, PHYSICAL, AND OPTICAL PROPERTIES

74   Kangite occurs as four irregular to subhedral grains, 1 to 4 μm in size, which

75 constitute the type material (Fig. 2). In the optically thick section (150 μm in thickness),

76 kangite is opaque. Color, streak, luster, hardness, tenacity, cleavage, fracture, density and

77 refractive index were not determined because of the small grain size. Given the large extent

78 of solid solution in the natural material and its cation deficient stoichiometry, it is unlikely

79 that these properties are close to those of synthetic Sc_2O_3. The density, calculated from its

80 crystal structure and the empirical formula, is 3.879 g/cm^3, which is similar to those of Sc_2O_3

81 (3.86) and panguite (3.75), but lower than those of TiO_2 (4.59) and Ti_2O_3 (4.23). Kangite is

82 not cathodoluminescent under the electron beam in an SEM and we observed no crystal

83 forms or twinning. Visible light fluorescence can be excited by light of 514.5 nm; we did not

84 check for fluorescence using alternative wavelengths.

85

CHEMICAL COMPOSITION

87   Chemical analyses of kangite (on the two leftmost grains in Fig. 2) and associated

88 minerals were carried out using a JEOL 8200 electron microprobe (WDS: 15 kV; 5 nA and

89 25 nA; beam in focused mode) interfaced with the Probe for EPMA program from Probe

90 Software, Inc. Possible interferences on peak position and background position were checked

91 and corrected for all measured elements based on WDS scans and using the Probe for EPMA;

92 on-peak interferences of Ti$K\alpha$ by Sc, V$K\alpha$ by Ti and Y, Cr$K\alpha$ by V, Er$L\alpha$ by Tb, Ho$L\alpha$ by

93 Gd, La$L\alpha$ by Nd, Ce$L\alpha$ by Ti and V, and Nd$L\alpha$ by Ce were corrected. Standards for the

94 analysis were TiO_2 (Ti$K\alpha$, O$K\alpha$), ScPO$_4$ (Sc$K\alpha$), zircon (Zr$L\alpha$), anorthite (Ca$K\alpha$, Al$K\alpha$,

95 Si$K\alpha$), YPO$_4$ (Y$L\alpha$), forsterite (Mg$K\alpha$), fayalite (Fe$K\alpha$), DyPO$_4$ (Dy$L\alpha$), ErPO$_4$ (Er$L\alpha$),

96 GdPO$_4$ (Gd$L\alpha$), TbPO$_4$ (Tb$L\alpha$), HoPO$_4$ (Ho$L\alpha$), ThO$_2$ (Th$M\alpha$), V_2O_3 (V$K\alpha$), Cr_2O_3 (Cr$K\alpha$),

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97   $LaPO_4$ (La$L\alpha$), $CePO_4$ (Ce$L\alpha$), $NdPO_4$ (Nd$L\alpha$), $SmPO_4$ (Sm$L\alpha$), and $YbPO_4$ (Yb$L\alpha$).

98   Quantitative elemental microanalyses were processed with the CITZAF correction procedure

99   (Armstrong 1995) and analytical results are given in Table 1. No other element with an

100 atomic number exceeding 4 was detected by WDS scans at 15 kV, 25 nA and 300 nA. In

101 particular, none of the light rare earth elements (LREE) nor Yb was detected in kangite or in

102 associated perovskite and davisite; detection limits for these elements at 99% confidence

103 were 0.03 wt% for Sm and 0.04 wt% for La, Ce, Nd, and Yb. On-peak WDS X-ray mapping

104 of Sc, Zr, Y, and Dy in ACM-3 (Fig. 3) was carried out at 15 kV and 100 nA, counting for

105 500 ms per pixel. The 250 x 320 pixel maps were collected using a 0.5 μm step size and

106 without a background correction.

107   The empirical formula of type kangite as analyzed by EPMA, based on three oxygens,

108 is $[(Sc_{0.53}Al_{0.19}Y_{0.07}V_{0.02}Gd_{0.01}Dy_{0.01}Er_{0.01})^{3+}_{\Sigma 0.84}(Ti_{0.63}Zr_{0.13}Si_{0.04})^{4+}_{\Sigma 0.80}$

109 $(Mg_{0.11}Ca_{0.10}Fe_{0.02})^{2+}_{\Sigma 0.23}\square_{0.13}]_{\Sigma 2.00}O_3$, where the oxidation states of Ti, V, and Fe are

110 assumed to be 4+, 3+, and 2+, respectively. Oxygen analyses by EPMA (at 15kV and 25 nA,

111 using LDE1 crystal for O$K\alpha$ measurement and synthetic TiO_2 as standard) in both kangite

112 and perovskite support Ti^{4+} (*versus* Ti^{3+}) in kangite, as shown in Table 1 where leftover O in

113 kangite (also perovskite) is roughly one standard deviation of the measured oxygen content

114 when all Ti is assigned to 4+. If all Ti is assumed to be 3+, then leftover oxygen in kangite is

115 3.4 wt% (i.e., an order of magnitude higher than the analytical error). We cannot reject the

116 possibility that minor Ti is trivalent as 8 % of the Ti in the kangite analysis in Table 1 would

117 be Ti^{3+} if the measured oxygen content is used to calculate Ti^{3+}/Ti^{4+} (contamination from

118 nearby davisite, which is Ti^{3+}-enriched (Ma and Rossman 2009b), does not significantly

119 affect this calculation). Nevertheless, EPMA analyses clearly indicate that Ti in kangite is

120 dominantly 4+. We cannot be certain of the valence for Fe or V because the concentrations

121 are too low. Some of the Fe in kangite could be ferric as alloys in Allende refractory

122 inclusions were often oxidized to magnetite during low temperature metasomatism (Blum et

123 al. 1989) and some of the V could be divalent as roughly half of the V in clinopyroxene and

124 spinel from Ca-, Al-rich inclusions from Allende is V^{2+} (Simon et al. 2007; Paque et al.

125 2010). Changing the assigned valences for Fe and/or V has a negligible effect on the inferred

126 crystallographic properties and no effect on the nomenclature of kangite or our conclusions

127 regarding origin. The apparent Si content in kangite is likely derived from the surrounding

128 davisite, because of the small grain size. If all Si and associated cations in the form of

129 surrounding davisite are removed, kangite shows a formula of

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130    $[(Sc_{0.54}Al_{0.16}Y_{0.07}V_{0.03}Gd_{0.01}Dy_{0.01}Er_{0.01})^{3+}_{\Sigma 0.83}(Ti_{0.66}Zr_{0.13})^{4+}_{\Sigma 0.79}(Mg_{0.11}Ca_{0.06}Fe_{0.02})^{2+}_{\Sigma 0.19}\square_{0.19}$

131    $]_{\Sigma 2.00}O_3$. Kangite is much more Ti- and Sc-rich than previously reported zirconias and is

132   more Sc-rich than panguite (Fig. 4). Based on EPMA, kangite exhibits an ultrarefractory rare

133   earth element (REE) pattern in which most of the heavy REE (HREE) are greatly enriched

134   relative to the LREE and Yb is depleted relative to the other HREE (concentrations of La, Ce,

135   Nd, Sm, and Yb are all below EPMA detection limits, 0.03-0.04 wt%) (Fig. 5). The general

136   formula for kangite is $(Sc,Ti,Al,Zr,Mg,Ca,\square)_2O_3$, or $(Sc,Ti,Al,Zr,Mg,Ca)_{1.8}O_3$, where Sc^{3+} is

137   the dominant trivalent component and the trivalent cations are dominant in the cation sites

138   without indications for cation ordering. The IMA-approved dominant-valency rule (Hatert

139   and Burke 2008) is applied here to designate this oxide as a new Sc mineral. The ideal end-

140   member formula is Sc_2O_3.

141   Kangite occurs within an aggregate of 2-12 μm diameter crystals of davisite, whose

142   Sc_2O_3 content ranges from as high as 17.66 wt% in portions of the inclusion near the spray of

143   kangite and perovskite crystals, to as low as 8.05 wt% near the inclusion-matrix boundary

144   and in the two lower lobes of the inclusion (the lobe containing the "spinel" label in Fig. 1

145   and the smaller lobe above and to the left of it; see also the Sc X-ray map in Fig. 3). Davisite

146   in the central region surrounding kangite and perovskite has a mean composition of

147    $Ca_{0.98}(Sc_{0.52}Ti^{3+}_{0.17}Mg_{0.14}Ti^{4+}_{0.09}Zr_{0.04}V^{3+}_{0.02}Y_{0.02}Al_{0.01}Fe^{2+}_{0.01})(Si_{1.00}Al_{1.00})O_6$, where

148   partitioning of Ti^{3+} and Ti^{4+} is based on a stoichiometric formula unit containing 4.00 cations

149   and 6 oxygens. High Sc davisite is HREE enriched (LREE are below detection limits) but

150   concentrations are a factor of several to an order of magnitude lower than in perovskite and

151   kangite. Low Sc davisite is also lower in Zr and HREE than high Sc crystals, showing an

152   average formula of $Ca_{0.98}(Sc_{0.30}Ti^{3+}_{0.19}Mg_{0.31}Ti^{4+}_{0.08}$

153    $Al_{0.07}Zr_{0.02}V^{3+}_{0.02}Y_{0.01}Fe^{2+}_{0.01})(Si_{1.20}Al_{0.80})O_6$. If kangite and nearby davisite equilibrated with

154   each other (although this may not have been the case, as discussed below), the compositions

155   (Table 1; Fig. 3) imply that Zr, V, Y and the REE are strongly partitioned into kangite

156   relative to davisite and Ca and, to a lesser extent, Al in davisite relative to kangite; the Ti

157   oxide panguite displays similar partitioning relationships with associated davisite (Ma et al.

158   2012). Note that about two-thirds of the Ti in davisite is inferred to be trivalent while

159   coexisting kangite contains little if any Ti^{3+}. One possible interpretation of this observation is

160   that kangite strongly preferred Ti^{4+} and discriminated against Ti^{3+} relative to davisite.

161   However, we argue below that kangite is the low temperature oxidation product of a high

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162   temperature Ti^{3+}-rich phase. Relative concentrations of cations were not significantly

163   affected but the additional oxygen was accommodated through the transformation of Ti^{3+} to

164   Ti^{4+}.

165   Perovskite in the kangite type example (Figs. 1-2) is Y-rich (Table 1) but Zr-poor

166   (~0.1 wt %), with a formula of $(Ca_{0.82}Y_{0.08}Dy_{0.03}Gd_{0.02}Sc_{0.02}Fe_{0.01}Er_{0.01}V_{0.01})(Ti_{0.94}Al_{0.02})O_3$.

167   As in kangite, the perovskite is HREE enriched with concentrations of LREE below EPMA

168   detection limits (Table 1; Fig. 5). Perovskite with similar REE abundances described by

169   Weber and Bischoff (1994) is relatively Zr-rich (ZrO_2 4 wt%). Associated spinel (Fig. 2) is

170   Fe-rich (FeO 11.22 wt%) with 0.42 wt% TiO_2, 0.38 wt% V_2O_3, and 0.30 wt% Cr_2O_3 (Table

171   1), showing a formula of $(Mg_{0.79}Fe_{0.24})(Al_{1.95}Ti_{0.01}V_{0.01}Cr_{0.01})O_4$. We note that stoichiometry

172   considerations require $Fe^{2+} >> Fe^{3+}$ for this phase (i.e., the spinel is hercynitic). The valence

173   state of Ti in the spinel, which can be either Ti^{3+}- or Ti^{4+}-enriched, at least in type B1

174   inclusions (Paque et al. 2010), is unknown. Overall, V-Ti-Cr concentrations are higher than

175   for most reported spinels from meteoritic inclusions in carbonaceous chondrites (e.g.,

176   Connolly and Burnett 1999; Connolly et al. 2003) but they are not diagnostic because

177   similarly enriched compositions, although rare, are occasionally encountered in wide variety

178   of inclusion types including fine-grained (Krot et al. 2004), compact type A (Srinivasan et al.

179   2000), fluffy type A (Allen et al. 1978), and type B1 inclusions (Wark and Lovering 1982; El

180   Goresy et al. 1985; Armstrong et al. 1987).

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182   **CRYSTALLOGRAPHY**

183

184   *EBSD AND SYNCHROTRON MICRO-LAUE DIFFRACTION*

185   EBSD analyses at a submicrometer scale were performed on the vibration-polished

186   section using methods described in Ma and Rossman (2008a, 2009a). An HKL (now Oxford)

187   EBSD system on a Zeiss 1550VP scanning electron microscope was used for these

188   measurements and operated at 20 kV and 6 nA in a focused beam configuration with a 70º

189   tilted stage and variable pressure (25 Pa) mode, which allows the study of uncoated

190   specimens. EBSD patterns of the kangite grains were indexed against structures of synthetic

191   Sc_2O_3 (Schleid and Meyer 1989), $ScTiO_3$ (Shafi et al. 2012), Sc_2TiO_5 (Kolitsch & Tillmanns

192   2003), Ti_2O_3 (Vincent et al. 1980), and perovskite $CaTiO_3$ (Liu & Liebermann 1993), and the

193   minerals panguite $(Ti^{4+},Sc,Al,Mg,Zr,Ca)_{1.8}O_3$ (IMA 2010-057; Ma et al. 2012), and

194   tazheranite $(Zr,Ti,Ca)O_{1.75}$ (cubic zirconia; Rastsvetaeva et al. 1998). Among these, the

195   patterns can be indexed using a bixbyite-type structure (Sc_2O_3, $ScTiO_3$), a bixbyite-type

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196   related structure (panguite), and a fluorite-type structure (tazheranite). Since the bixbyite

197   structure can be derived from a fluorite-structured oxide through a systematic removal of

198   oxygens, it follows that the EBSD data suggest a fluorite- or defective fluorite-structure.

199   Synchrotron micro-Laue diffraction on one kangite domain was carried out at the

200   34ID-E undulator beamline of the Advanced Photon Source in the Argonne National

201   Laboratory using a 250×400 nm^2 polychromatic X-ray beam and an array of Perkin-Elmer

202   amorphous Si area detectors, using methods described in detail by Ma et al. (2012) in our

203   study of the newly discovered Sc-bearing Ti-oxide panguite. An energy scan (energy range

204   16 to 27 keV, 1 eV steps) of the primary beam yielded a set of 16 reflections, which were

205   used for a reverse Monte Carlo optimization (Endeavour 1.4; Puetz et al. 1999) with the

206   Sc_2O_3 C-type (bixbyite-type) structure as the initial configuration. The rMC optimization

207   converged to $R_{Bragg} = 0.079$ for the cubic bixbyite-type structure (see Deposited Item).

208   Subsequently we used SHELXL (Sheldrick 2008) for refinement. Isotropic atomic

209   displacement (U_{iso}) values, site occupancy factors (SOFs) of Sc1, Sc2, and x,y,z coordinates

210   for the cation and oxygen sites are given in Table 2. Refinement of the U_{iso} values, SOFs and

211   fractional coordinates was conducted in sequential steps.

212   Kangite shows a cation-deficient $Ia\overline{3}$ bixbyite-type structure with unit cell dimension

213   $a = 9.842(1)$ Å, $V = 953.3(1)$ Å^3, $Z = 16$. The EBSD pattern (Fig. 6) is an excellent match to

214   the computed EBSD pattern obtained using the cell parameter of the cubic structure from the

215   synchrotron micro-diffraction analysis with resulting mean angular deviations as low as 0.35.

216   X-ray powder-diffraction data (Table 3, in Å for Cu$K\alpha1$, in Bragg-Brentano geometry) were

217   calculated using PowderCell (Kraus and Nolze 1996) version 2.4. Cation-cation distances in

218   kangite are around 2.6% larger than in synthetic Sc_2O_3 (Schleid and Meyer 1989). Isotropic

219   thermal displacement factors of the 8a and the 24d cations are similar, 0.017 and 0.015 in

220   synthetic Sc_2O_3 (Schleid and Meyer 1989) versus 0.012 and 0.009 in kangite (Table 2),

221   respectively. However, thermal displacement of oxygen is significantly larger in kangite than

222   in synthetic Sc_2O_3: 0.16 versus 0.019 Å^{-2}. We relate this observation to another important

223   difference between the structures of kangite and synthetic pure Sc_2O_3. In both kangite and

224   pure Sc_2O_3, cations residing at site 8a have six next neighbor anions, although cation-anion

225   distances are 5% shorter in kangite than in pure Sc_2O_3. In synthetic Sc_2O_3 the cation on site

226   24d has six-fold coordination with Sc-O distances ranging from 2.08 to 2.17 Å, as expected

227   for bixbyite-type phases (Wyckoff 1960). In kangite, however, two apices of the 24d centered

228   polyhedron are clearly beyond Sc-O bond distances, leaving Sc with an apparent four-fold

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229   coordination. The four shortest cation-O distances range from 1.8 to 2.2 Å with the other two

230   at 3.0 and 3.5 Å. Obviously, bond orbital distributions still require a 6 - 8 fold coordination of

231   the major cations (Sc, Ti, Zr , etc.). These unusual observations can be explained by the high

232   density of cation vacancies in kangite and the fact that site occupancies for the 8a and 24d

233   sites are quite different. The 24d site has only 60% occupancy whereas the 8a site has 80%

234   occupancy. It is therefore likely that cations in the 8a site attract O closer in unit cells for

235   which the 24d site is empty than in those for which 24d is occupied. In the averaged structure

236   sampled by the micro-Laue measurements, this results in an overall shift of the O-atom

237   position away from the 24d site leaving the latter with an apparent incomplete coordination.

238   This interpretation is supported by the unusually large thermal displacement factor of O,

239   which is almost a factor of ten larger than in pure Sc_2O_3 (see above). In other words, this

240   large thermal displacement factor convolutes the static disorder of O atomic positions in

241   kangite. Such disorder can, in principle, be modeled by partial occupancies of multiple 48e

242   sites for O. However, such further refinement would require more unique reflections than are

243   available in our data set.

244   The structural relationships between kangite and panguite are very interesting because

245   of the similar compositions. Both phases are Ti-, Sc-rich oxides, whose compositions are well

246   expressed using a pseudobrookite-type formula M_3O_5, but they reveal a bixbyite-type (M_2O_3)

247   or related structure. Kangite, which contains more Sc and significantly higher HREE

248   contents, has a bixbyite-type structure, whereas panguite shows a reduction in symmetry from

249   bixbyite-type $Ia\overline{3}$ to *Pbca*. In bixbyite and kangite, the cations assume two Wykhoff sites, 8a

250   and 24d, whereas the anion resides on the general position 48e. The cubic bixbyite structure

251   is related to the structure of panguite by a group-subgroup chain $Ia\overline{3} \rightarrow Ibca \rightarrow Pbca$ where

252   all atoms occupy the general site 8c (Aroyo et al. 2006). The reduced crystal symmetry of

253   panguite is the result of lattice relaxation due to the large number of vacancies and large

254   concentration of cations whose ionic radii are smaller than expected for a bixbyite-type structure.

255   This has been discussed in detail in Ma et al. (2012). Kangite has similarly large cation deficiency

256   but a larger concentration of REE elements, all of which establish end-member oxides in the

257   bixbyite structure. It is this higher concentration of large cations that stabilizes the bixbyite

258   structure for kangite. Cooling rates during the formation process may also play a role. However,

259   this can only be assessed by experimental studies on synthetic equivalents of kangite and

260   panguite.

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262 *RAMAN SPECTROSCOPY*

263 Raman spectroscopic microanalysis was carried out using a Renishaw M1000 micro-

264 Raman spectrometer system on kangite domains of the sample in polished section, using the

265 methods described in Ma and Rossman (2008a, 2009a). Approximately 5 mW of 514.5 nm

266 laser illumination (at the sample) focused with a 100× objective lens provided satisfactory

267 spectra. The spot size was about 2 μm. The spectrum of kangite is characterized by intense

268 fluorescence features, similar to those of nearby perovskite grains, as shown in Figure 7. The

269 dominant Raman feature of synthetic Sc_2O_3 at 419 cm^{-1} (Ubaldini and Carnasciali 2008) is

270 nearly invisible. The intense fluorescence features are due to significant amounts of

271 fluorescent *REE* elements in both kangite and perovskite (Table 1). Because features in the

272 Raman spectra arise from intense optical fluorescence due to the REE elements, there are no

273 identifiable Raman shifts and, hence, the spectra provide no information about the crystal

274 structure of the host phase.

275

276 **DISCUSSION**

277 Kangite is a new Sc-, Ti-rich oxide, (Sc,Ti,Al,Zr,Mg,Ca,□)$_2$O$_3$, with a $Ia\overline{3}$ bixbyite-

278 type structure, and a new member of the bixbyite group, which already contains bixbyite

279 (Mn_2O_3), avicennite (Tl_2O_3) and yttriaite-(Y) (Y_2O_3). It is the first mineral with a bixbyite-

280 type structure to be found in a meteorite. Kangite also joins a variety of Zr-, Y-, and Sc-rich

281 oxides and silicates, including allendeite, tazheranite, zirconolite, panguite, thortveitite,

282 lakargiite, eringaite, and davisite, that have been reported in refractory inclusions from

283 carbonaceous chondrites (Allen et al. 1980; Hinton et al. 1988; El Goresy et al. 2002; Ma and

284 Rossman 2008b, 2009b; Ma et al. 2009, 2011; Ma 2011; Ma 2012; Ma et al. 2012). Each of

285 these phases is a potential sensor of environment and kangite has the added advantage of

286 being heavy rare earth enriched and, therefore, potentially sensitive to condensation and

287 evaporative processes.

288 The juxtaposition of kangite, which has little if any Ti^{3+}, within an aggregate of

289 davisite crystals whose Ti is largely trivalent, presents a challenge for understanding the

290 origin of kangite. There are three basic possibilities: (1) kangite formed or equilibrated in an

291 oxidizing environment separate from the reducing environment necessary to produce davisite

292 and was later transported to the davisite (or vice versa); (2) davisite and kangite both form

293 under reducing conditions but kangite discriminates against Ti^{+3} in much the same way that

294 perovskite, which is also present in this inclusion, does; (3) kangite originally formed as a

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295   Ti^{3+}-enriched phase that was incorporated into the davisite aggregate but these original grains

296   were later oxidized at low temperatures (too low to affect the davisite) to form kangite.

297   Phase equilibria place basic constraints on the stability of a mineral and the conditions

298   under which it may have formed. For kangite, the most relevant binary system under

299   oxidizing conditions is Sc_2O_3-TiO_2 but the phase relations of Sc_2O_3-TiO_x-bearing systems in

300   general and of bixbyite-structured oxides within these systems in particular are poorly

301   constrained. The high temperature phase diagram of Magunov and Magunov (2002) for the

302   system Sc_2O_3-TiO_2 shows a solubility of only a few mole % TiO_2 in the terminal Sc_2O_3 solid

303   solution (their data constrain it to < 10 mole%) with greater amounts of TiO_2 generating

304   Sc_2TiO_5 up to the melting point of that compound at 1347°C. Although they did not note it,

305   the compound $Sc_4Ti_3O_{12}$ (e.g., Lyashenko et al. 2004) also appears to be stable in this system

306   at high temperatures. There are also some constraints on phase stabilities for compositions

307   within the quaternary Sc_2O_3- TiO_2-Y_2O_3-ZrO_2 (e.g., Tao and Irvine 2002) but the

308   experimentally examined compositions are far richer in Y+Zr ($\geq$65 mole % of the cations for

309   Tao and Irvine's study) than in kangite (~10%; Fig. 4). Kangite has not been synthesized to

310   our knowledge but many trivalent end-member oxides are known to assume a bixbyite

311   structure, including Sc_2O_3, Y_2O_3, trivalent oxides of the rare earths, and In_2O_3. Available data

312   for Sc_2O_3-TiO_2 imply that a bixbyite structured scandian oxide as TiO_2-rich as kangite (molar

313   Ti/Sc ~1.2) is not a stable high temperature phase under oxidizing conditions relative to a

314   Sc_2TiO_5- or $Sc_4Ti_3O_{12}$-bearing phase assemblage. This argues against scenario (1) given at

315   the beginning of this section and for a low temperature origin. If kangite is a high temperature

316   phase produced under oxidizing conditions, then one or more of the other cations present in

317   significant concentrations (i.e., Al, Zr, Mg, and/or Ca) must have stabilized the bixbyite

318   structure.

319   It is important to consider the possible role of Ti^{3+} in the origin of kangite, both from

320   the perspective of whether or not kangite can accommodate Ti^{3+} (e.g., scenario 2) and what

321   the nature and stability of a Ti^{3+}-enriched precursor would have been (scenario 3). The

322   average ionic radius of trivalent cations in kangite is 0.70 Å and, if Si is removed from the

323   formula in the form of davisite (i.e., all Si in the kangite analysis is due to contamination of

324   the activation volumes for EPMA by the surrounding davisite), then the average ionic radius

325   is 0.67 Å. Moreover, trivalent cations present in significant concentrations (Al, Sc, Y) have

326   ionic radii ranging from 0.53 to 0.89 Å. The ionic radius of Ti^{3+} is 0.67 Å, near the average,

327   which implies that there are no large size-related energetic penalties associated with the

328   substitution of Ti^{3+} into kangite. Thus, scenario (2) is unlikely. Kangite discriminated against

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329   Ti^{3+} because there was little or none to be had at the time it formed. Kangite formed (or

330   equilibrated) in an oxidizing environment separate from the one that produced the davisite.

331   If kangite is the oxidized form of a Ti^{3+}-enriched precursor (scenario 3), then phase

332   relations in the system Sc_2O_3-Ti_2O_3 are pertinent to the origin of the precursor but these are

333   even less well constrained than for Sc_2O_3-TiO_2. Ti_2O_3, which takes on a corundum-type

334   structure ($R\bar{3}c$), can be synthesized with up to 4 mole % Sc_2O_3 (Chandrashekar et al. 1974)

335   and the double oxide $ScTi^{+3}O_3$, which has a bixbyite-type structure, is readily synthesized at

336   high temperatures under reducing conditions (Reid and Sienko 1967). The solubility of Ti_2O_3

337   in a terminal Sc_2O_3 solution is unknown but, given that bixbyite-type structures tend to be

338   mostly sensitive to ionic radius for a potential substituting cation, it seems likely that the

339   solubility is significantly greater than that of Sc in tistarite (Ti_2O_3). Even these limited

340   observations place an important constraint on the origin of kangite. A kangite precursor

341   could, in principle have been an M_2O_3 oxide but, given the low solubility of Sc in Ti_2O_3, it

342   was not tistarite.

343   Although there is a paucity of phase equilibrium data for kangite composition oxides

344   and Ti^{3+}-enriched analogs, there is a substantial literature concerning the solubility

345   relationships and energetics of solid solutions of bixbyite-type structured oxides. Systems

346   involving In_2O_3 are the most heavily studied because of their use in energy efficient windows,

347   flat screen panel displays and an assortment of photovoltaics but there are enough data on

348   enough systems (e.g., Busker et al. 1999; Freeman et al. 2000; Saha et al. 2002; Mason et al.

349   2003; Levy et al. 2007; Hoel et al. 2010) to allow for the expression of some general

350   principles regarding the substitution of cations into a bixbyite structured end-member M_2O_3

351   oxide such that the $Ia\bar{3}$ space group is retained: (1) for an aliovalent substitution (i.e., a 3+

352   cation substituting for a 3+ cation), cations with ionic radii similar to those of the host are

353   energetically favored; (2) substitution of a single type of divalent or tetravalent cation for a

354   3+ host is compensated by oxygen interstitials or cation vacancies (for kangite this would

355   likely be via cation vacancies); (3) co-doping of 4+ and 2+ cations substantially enhances the

356   solubility of both cations relative to the solubility of either by itself; and (4) the solubility of

357   co-doped 4+ and 2+ cations is maximized when the average ionic radius of the two cations

358   approaches that of the host.

359   Consider a reduced precursor to kangite (scenario 3) in light of the above four

360   principles. We begin with the premise that Si is a contaminant from davisite, although it is

361   possible that Si is soluble in small amounts in kangite. As shown above, removing the Si by

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362   subtracting davisite and renormalizing to a 3 oxygen basis leads to the kangite formula:

363    $[(Sc_{0.54}Al_{0.16}Y_{0.07}V_{0.03}Gd_{0.01}Dy_{0.01}Er_{0.01})^{3+}_{\Sigma0.83}(Ti_{0.66}Zr_{0.13})^{4+}_{\Sigma0.79}(Mg_{0.11}Ca_{0.06}Fe_{0.02})^{2+}_{\Sigma0.19}\square_{0.19}$

364    $]_{\Sigma2.00}O_3$. This formula has slightly lower Al and Ca (and no Si) than the measured kangite

365   composition as given in Table 1 because these cations are in much greater abundance in

366   davisite than in kangite. There are 0.79 quadrivalent cations in this formula unit but only 0.19

367   divalent cations, which means that there are far more 4+ cations than can be accommodated

368   through co-doping of 2+ and 4+ cations. This is equivalent to saying that there are far more

369   Ti^{4+} cations than can be accounted for through co-doping. As an end-member model, we

370   assume that all 4+ cations are co-doped with 2+ cations in the kangite precursor and that all

371   remaining Ti in the kangite precursor was trivalent. This yields a formula unit of

372    $[(Ti_{0.61}Sc_{0.53}Al_{0.19}Y_{0.06}V_{0.02}Gd_{0.01}Dy_{0.01}Er_{0.01})^{3+}_{\Sigma1.44}(Ti_{0.05}Zr_{0.14})^{4+}_{\Sigma0.19}(Mg_{0.11}Ca_{0.06}Fe_{0.02})^{2+}_{\Sigma0.19}$

373    $]_{\Sigma2.00}O_3$ for the kangite precursor. Note that this phase has an even higher Ti^{+3}/Ti^{+4} ratio (12)

374   than does davisite (2). Of course, intermediate formulae can be constructed in which some

375   fraction of the Ti that is not co-doped with a divalent cation is accommodated as Ti^{+4} in the

376   precursor through cation defects or interstitial oxygen. Ti^{4+} (0.605 Å) has a significantly lower

377   ionic radius than does Sc (0.73 Å) or Ti^{3+} (0.67 Å) but the average ionic radius for a $Ca:Ti^{4+}$

378   co-doping couple is higher (0.80 Å) than the average ionic radius for the trivalent cations

379   though still smaller than that of Y (0.89 Å), which is present in kangite in similar

380   concentrations. Perhaps Al, which has a much lower ionic radius (0.53 Å) than those of Sc or

381   Ti^{3+}, partially stabilizes the structure for $Ca:Ti^{4+}$ co-doping by reducing the mean ionic radius

382   for the mineral. Connecting the proposed precursor composition to specific redox conditions

383   would require additional experimentation but we can say that Ti^{3+} enriched precursors to

384   kangite are consistent with reducing conditions and that they may have formed in an

385   environment similar to or directly related to the one that produced the host davisite. The

386   structure of the kangite precursor is uncertain but the fact that cations of $Ti^{3+} \sim Sc^{3+}$ in the

387   davisite-corrected formula unit given above suggests the possibility that this may have been

388   an $ScTiO_3$ bixbyite- type phase with considerable solid solution towards various other

389   components. Alternatively, the inferred Ti:Sc ratio is fortuitous and the kangite precursor was

390   a terminal Sc_2O_3 solid solution. Both phases have a bixbyite-type structure. The kangite

391   precursor, which may well have been a high temperature condensate, was incorporated into

392   the host davisite aggregate but, at a presumably later time, the 0.6 cations of Ti^{3+} on a 3

393   oxygen basis, that was originally present, was oxidized to form 0.6 cations of Ti^{4+} and the

394   phase transformed into kangite. Shafi et al. (2012) showed that Ti^{3+} in $ScTi^{3+}O_3$ is readily

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395   oxidized at low temperatures to form a metastable intermediate with a stoichiometry of

396     $Sc_2Ti^{4+}_2O_7$, which has a defect fluorite structure. A similar process may have occurred with

397   the kangite precursor but this phase, having only half the Ti^{3+} present in the end-member

398     $ScTiO_3$ could only be oxidized to an overall M_3O_5 (i.e., pseudobrookite-like) stoichiometry

399   and it therefore assumed or retained the bixbyite structure, as observed for kangite. The

400   oxidation process must have occurred at a sufficiently low temperature so that the kangite, so

401   produced, did not break down to form other, more stable oxides and davisite was unaffected.

402   We can place some constraints on the conditions for this process through a consideration of

403   CAIs in Allende. Based on alloy-oxide equilibria, the alloys in Allende CAIs were oxidized

404   at temperatures in the vicinity of ~500°C under conditions about a log unit more oxidizing

405   than the iron-wüstite buffer (e.g., Blum et al. 1989). During this event, clinopyroxene was

406   unaffected but iron diffused into the centers of large, 40-60 µm diameter, spinel grains from

407   the core region of an Allende type B inclusion, hundreds of µm from the surface of the CAI

408   (Paque et al. 2007). Spinel in the kangite bearing inclusion described here is very iron rich

409   (11.2 wt % FeO) and it is likely that this Fe was introduced during the Allende metasomatic

410   event. Given the close proximity of kangite crystals (≤ 20 µm from the surface of the host

411   inclusion), the small grain size (2-12 µm) of the davisite (hence many grain boundaries that

412   could act as fast pathways for diffusion from the external medium outside the inclusion to the

413   surfaces of the kangite precursors), the small grain size of the kangite (1-4 µm grain sizes but

414   not more than ~2 µm thick; see Fig. 2), and the highly ferroan compositions of nearby and

415   kangite-contacting spinel in the same inclusion, it is virtually certain that the kangite

416   precursor would have been exposed to these oxidizing metasomatic conditions. If so, the low

417   concentration of Fe in kangite suggests that the solubility of Fe^{2+} was very low compared to

418   spinel exposed to virtually identical conditions (cf., Table 1). This is consistent with the

419   absence of exchangeable Ti^{4+} from other phases during the alteration process that would have

420   been necessary to charge balance the substitution of Fe^{2+} into kangite.

421   We conclude that kangite most likely formed as the low-temperature oxidation

422   product of a Sc-, Ti^{3+}-enriched oxide that formed under reducing conditions, presumably as a

423   condensate and probably with a bixbyite-type structure. Note that this high temperature

424   precursor, were it to be found, would be a new mineral. It would not be kangite because

425   cations of Ti^{3+} > Sc and it would not be tistarite because it would have a different structure.

426   This reduced kangite precursor was incorporated into an aggregate of davisite crystals along

427   with small amounts of perovskite and spinel and it was later oxidized to form kangite. It is

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428   possible that the oxidation event occurred prior to incorporation into the davisite aggregate

429   (i.e., the grains arrived as kangite crystals) but the most straightforward scenario is one in

430   which the same metasomatic event that introduced iron into spinels, including the ones shown

431   in Figures 1-2, and oxidized metal in Allende CAIs, also caused in situ oxidation of the

432   kangite precursor. If so, the composition of the kangite, except for oxygen and possibly Fe,

433   approximates that of the original precursor and, because there were ≤ 0.6 cations of Ti^{3+} per 3

434   oxygens in the original crystals, oxidation yielded a roughly M_3O_5 stoichiometry and a

435   bixbyite-type structure was retained.

436   Although we have emphasized the origin of kangite in this discussion, it is also

437   important to place the proposed Ti^{3+}-enriched precursor into a broader cosmochemical

438   context. Both kangite and perovskite in the inclusion described in this study are highly

439   enriched in HREE (Fig. 5) and this provides a key to understanding their origin. In general,

440   ultrarefractory inclusions are characterized by extraordinarily high HREE/LREE ratios and

441   negative Yb anomalies as shown in Figure 5. Only a handful of meteoritic inclusions with

442   ultrarefractory REE patterns have been described (e.g., Davis 1984; 1991; Simon et al. 1996;

443   El Goresy et al. 2002; Uchiyama et al. 2008) but Boynton (1975) proposed their existence

444   before any had been discovered based on thermodynamic modeling of high temperature

445   condensation. Moreover, the absence of isotopic mass fractionation in Ti and Mg in at least

446   one of these inclusions suggests that the ultrarefractory grains are condensates rather than

447   evaporative residues (Simon et al. 1996). Some meteoritic inclusions (described as Group II)

448   appear to have derived their REE budget via condensation from a reservoir that was depleted

449   in an ultrarefractory component. Group II inclusions are fairly common among CAIs and

450   especially common among fine-grained inclusions (Davis 1991; Hiyagon et al. 2011).

451   Ultrarefractory phases, including perovskite and the kangite precursor from this study, are

452   representatives of solid extracts from high temperature fractional condensation processes.

453   Although the occurrence of ultrarefractory material as original condensate grains is rare, its

454   effect is often observed through REE patterns of lower temperature condensates that are

455   missing an ultrarefractory component.

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626 **Table 1**. Mean electron microprobe analytical results for type kangite, associated perovskite,

627 spinel, and host davisite.

Constituent	kangite	perovskite	davisite next to kangite and perovskite	davisite near the edge	spinel
wt%	n=7[a]	n=6	n=6	n=2	n=6
TiO_2	36.6(4)[b]	51.2(3)	8.9(6)	9.2(7)	0.42(2)
Sc_2O_3	26.4(5)	0.8(2)	15(1)	9(1)	0.05(1)
ZrO_2	11.3(3)	0.13(5)	2.1(5)	1.1(3)	b.d.
Al_2O_3	7.0(2)	0.84(9)	22(2)	19.1(5)	65.75(7)
Y_2O_3	5.4(1)	6.3(1)	0.8(1)	0.68(3)	b.d.
CaO	3.9(2)	31.3(2)	23.2(4)	23.70(2)	0.15(2)
MgO	3.14(6)	b.d.[c]	2(1)	5.4(5)	21.2(1)
SiO_2	1.7(4)	b.d.	25(2)	31.1(7)	b.d.
V_2O_3	1.31(4)	0.64(4)	0.53(2)	0.52(4)	0.38(1)
FeO	0.8(6)	0.61(2)	0.40(7)	0.43(7)	11.22(7)
Cr_2O_3	0.09(2)	b.d.	b.d.	0.03(1)	0.30(1)
Dy_2O_3	1.8(1)	3.1(1)	0.30(7)	0.25(4)	n.a.[d]
Er_2O_3	0.92(5)	1.00(5)	0.10(5)	b.d.	n.a.
Gd_2O_3	0.60(4)	2.52(7)	0.18(9)	0.14(2)	n.a.
Ho_2O_3	0.40(2)	0.48(7)	b.d.	b.d.	n.a.
Tb_2O_3	0.18(7)	0.40(6)	b.d.	b.d.	n.a.
ThO_2	0.04(2)	0.40(6)	b.d.	b.d.	n.a.
O[e]	-0.3(2)	-0.3(2)			
Total	101.28	99.42	100.51	100.65	99.47

628
629 [a]Number of analyses.
630 [b]Numbers in parentheses represent one standard deviation of the mean for the n analyses
631 conducted on the phase.
632 [c]Below detection. Detection limits at 99% confidence are Mg 0.09 wt%, Si 0.08 %, Cr 0.07
633 %, Zr 0.05%, Y 0.06%, Si 0.02%, Er 0.10%, Ho 0.09%, Tb 0.08%, Th 0.03%.
634 [d]Not analyzed.
635 [e]Difference between oxygen measured by EPMA and value obtained from elemental
636 concentrations of cations as determined by EPMA in which a single valence (listed in the left
637 hand column) has been assumed for each of the oxides. The quoted uncertainty reflects only
638 the analytical error on the oxygen analysis.
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642   **Table 2**. Atom coordinates.
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	x/a	y/b	z/c	SOF	U_{iso}
Sc1	0.25	0.25	0.25	0.767(2)	0.012(3)
Sc2	0.9784(2)	0	0.25	0.590(1)	0.0093(3)
O	0.3207(6)	0.227(5)	-0.44(5)	1	0.16(9)

650 **Table 3**. Calculated X-ray powder diffraction data for kangite.
651

h	k	l	d [A]	I_{rel}
2	**1**	**1**	**4.0190**	**16**
2	**2**	**2**	**2.8419**	**100**
3	2	1	2.6311	1
4	**0**	**0**	**2.4612**	**10**
4	1	1	2.3204	5
4	2	0	2.2013	1
3	**3**	**2**	**2.0989**	**15**
4	2	2	2.0095	2
4	**1**	**3**	**1.9307**	**75**
5	2	1	1.7974	3
4	**4**	**0**	**1.7403**	**51**
4	3	3	1.6883	3
4	4	2	1.6408	1
6	1	1	1.5970	4
6	0	2	1.5566	1
5	**4**	**1**	**1.5191**	**29**
6	**2**	**2**	**1.4841**	**23**
6	1	3	1.4515	4
4	4	4	1.4210	2
5	4	3	1.3922	2
6	0	4	1.3652	1
7	2	1	1.3397	4
6	4	2	1.3155	1
6	1	5	1.2503	1
8	0	0	1.2306	4
8	1	1	1.2118	2
8	2	0	1.1938	1
6	5	3	1.1767	1
8	2	2	1.1602	1
8	3	1	1.1444	1
6	6	2	1.1293	6
8	0	4	1.1007	2
8	3	3	1.0869	1
8	2	4	1.0739	1
6	5	5	1.0613	2
6	6	4	1.0492	1
7	4	5	1.0374	1
7	6	3	1.0151	2
8	4	4	1.0045	5
9	4	1	0.9942	1
8	5	3	0.9942	2
8	6	0	0.9842	2
7	7	2	0.9745	1
8	2	6	0.9651	4
9	3	4	0.9559	1
10	2	2	0.9471	4
7	6	5	0.9384	1
8	5	5	0.9218	1

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705 **Deposited Item**.
706 List of observed and calculated normalized structure factor moduli of unique reflections.*
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h k l	F_o^2	F_c^2	$\sigma(F^2)/su$	$F_c/F_c(max)$	Resolution (Å)
2 6 8	92916.11	56643.00	1.77	0.575	0.97
4 4 10	52273.38	41034.36	0.97	0.489	0.86
0 6 10	27150.91	32576.42	0.93	0.436	0.84
0 0 10	55806.35	56775.83	0.17	0.576	0.98
4 4 8	168947.70	171334.06	0.14	1.000	1.00

716 *R_1 = 0.084 for 5 unique reflections after merging; $wR2$ = 0.139, GooF 0.875 (Sheldrick
717 2008).
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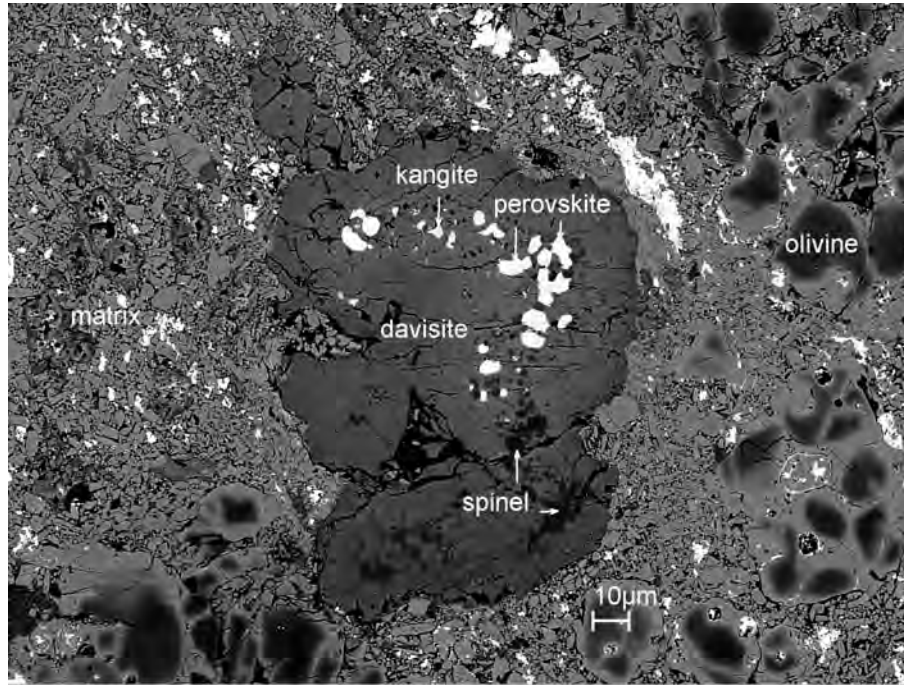
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724 **Figure 1**. BSE image of ultrarefractory inclusion ACM-3 in section USNM 7555 from the
725 Allende meteorite, where the type davisite (Ma and Rossman 2009b) and kangite (this study)
726 occur. Scale bar is 10 µm.
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729   (a)

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732   (b)
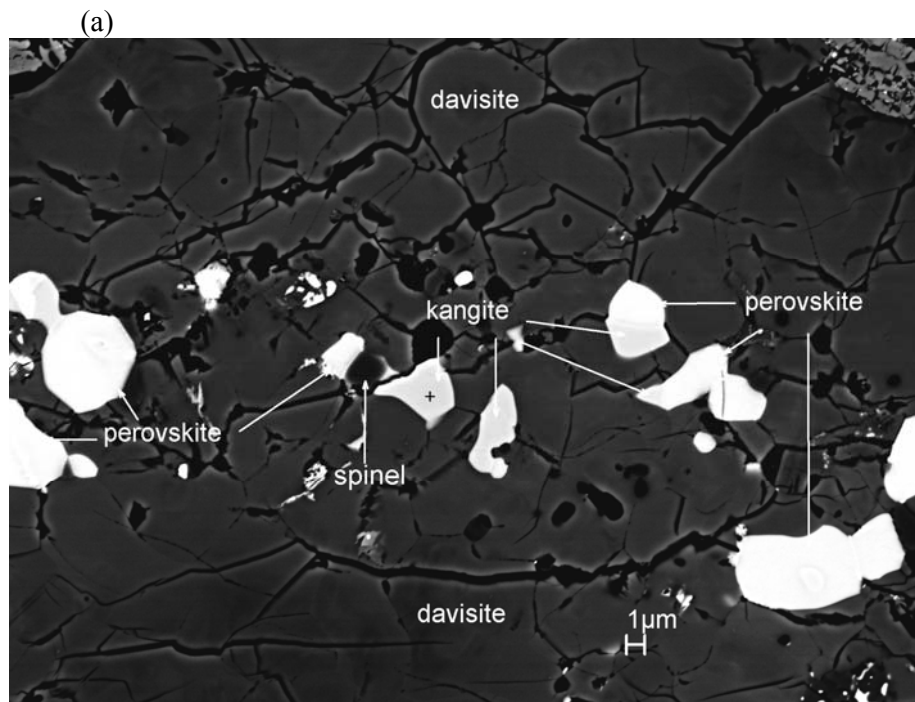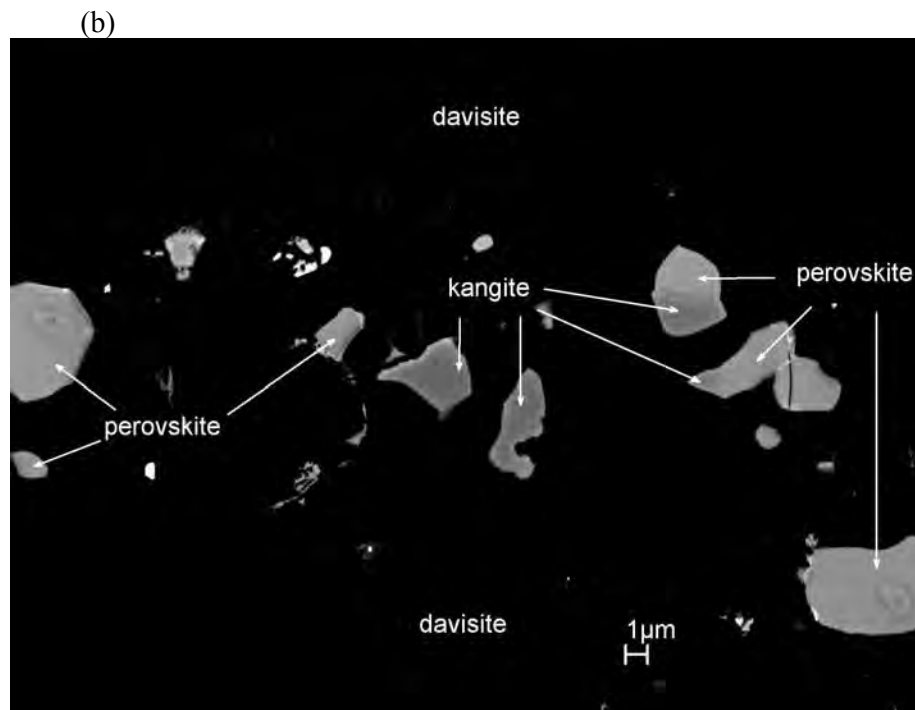
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735   **Figure 2**. Enlarged BSE images of ACM-3 with contrasts optimized to show kangite
736   microcrystals (type material) with perovskite and spinel in host davisite. The cross mark
737   shown in (a) indicates where the EBSD pattern (shown in Fig. 6) and the synchrotron micro-
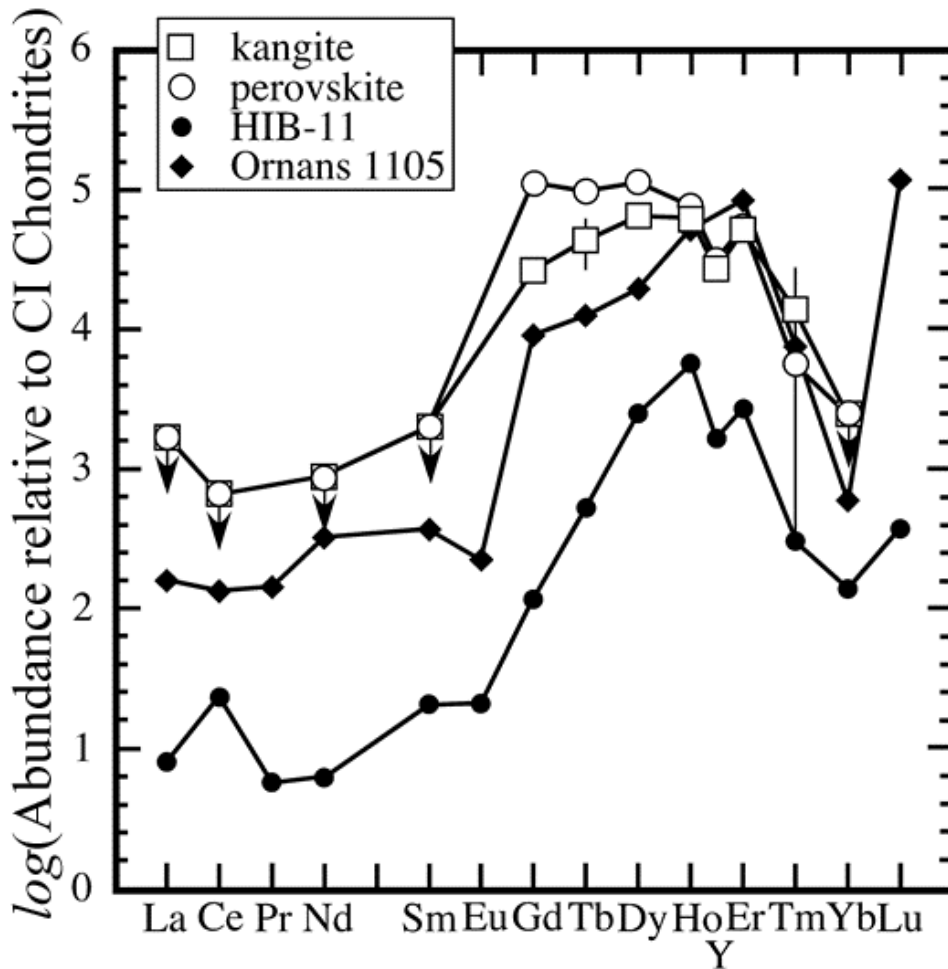738   Laue diffraction data were collected. Scale bar is 1 μm.
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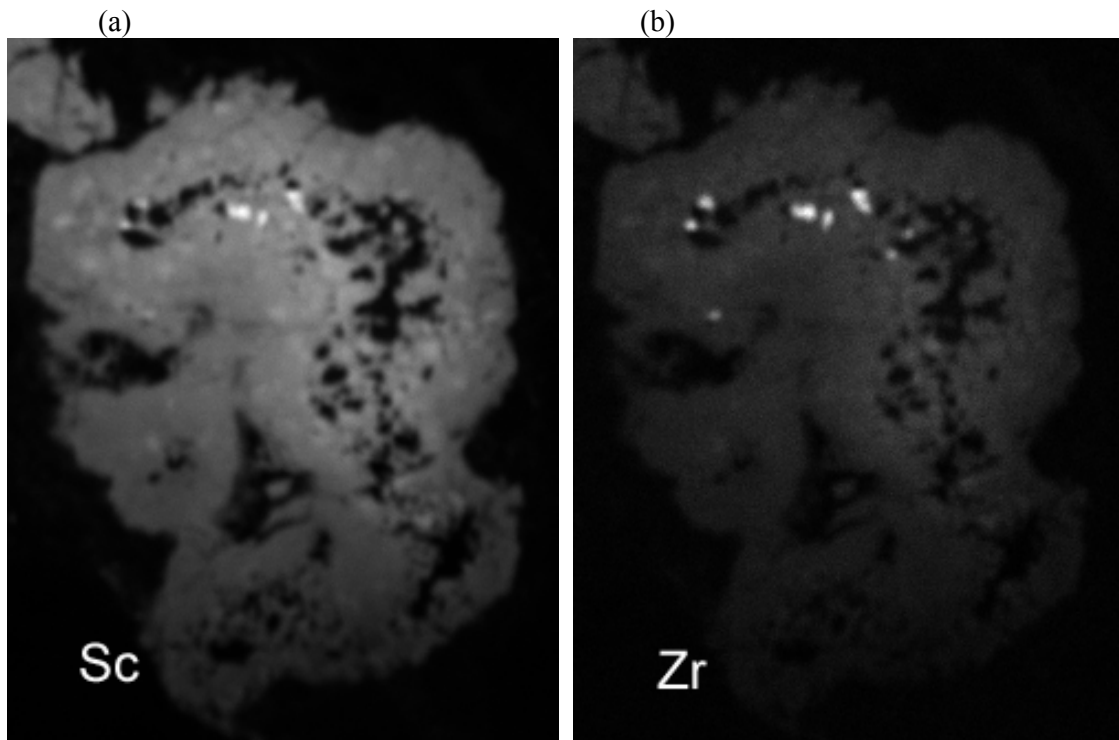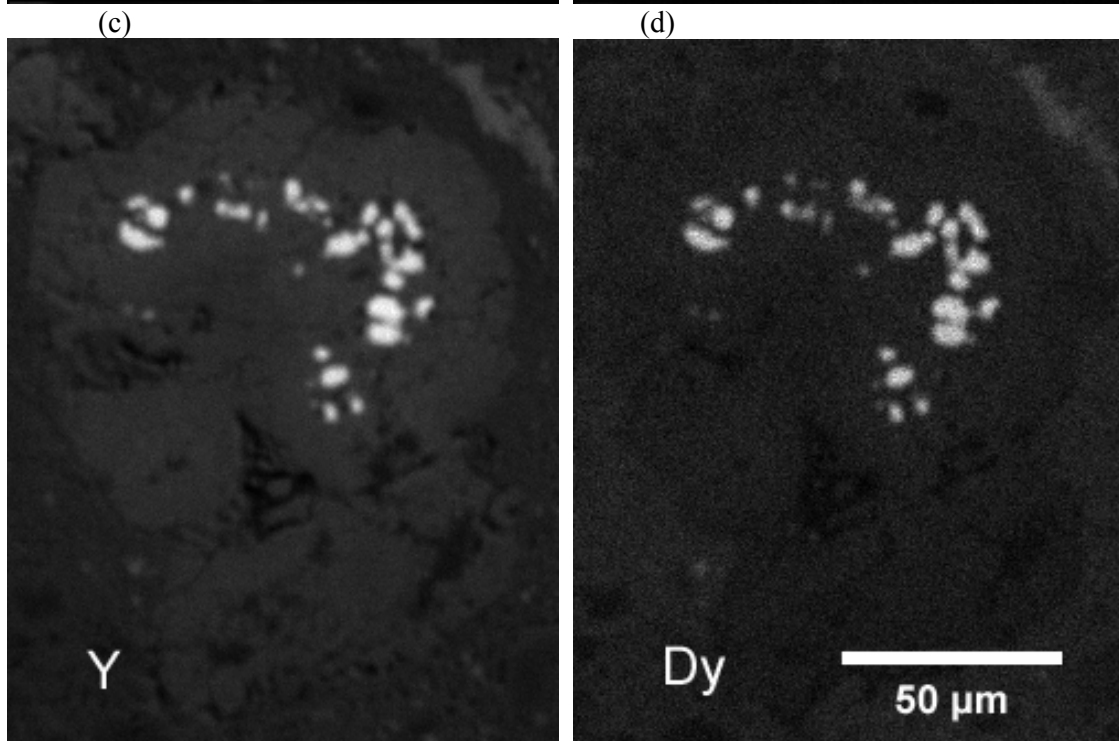
745
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747   **Figure 3**. Sc, Zr, Y, and Dy X-ray maps of ultrarefractory inclusion ACM-3. Scale bar is 50
748   μm.

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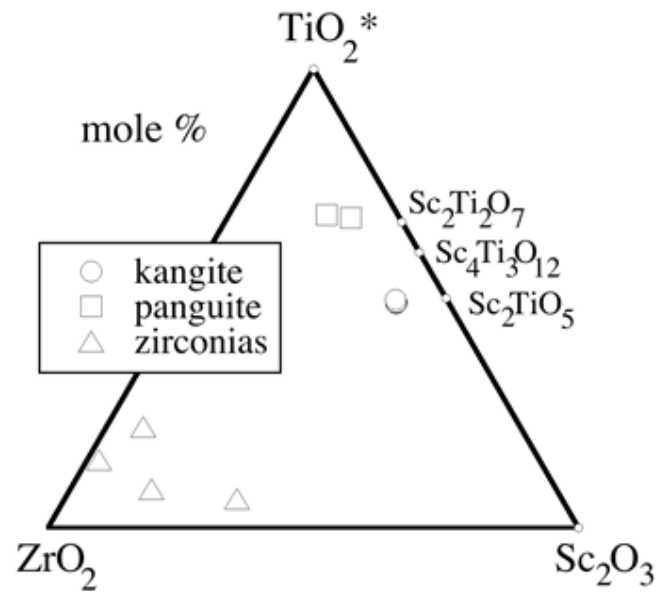
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753   **Figure 4.** Compositions in mole % of meteoritic Sc-, Zr-enriched oxides in terms of the
754   ternary Sc_2O_3 - TiO_2* (where all Ti is computed as TiO_2) - ZrO_2. These three oxides account
755   for 80-97% of cations in the zirconias and 70-74% of the cations in kangite and panguite, the
756   balance being mostly Al, Ca, Mg, and Y. Data are taken from Noonan et al. (1977), Lovering
757   et al. (1979), Hinton et al. (1988), Weber and Bischoff (1994), Ma et al. (2012), and this
758   study.
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766 **Figure 5.** Abundance of REE and Y relative to CI chondrites (Anders and Grevesse 1989) in
767 kangite and perovskite from ACM-3. Error bars for analyses from this study are standard
768 deviations on multiple analyses where larger than the symbols. Downward pointing arrows
769 indicate maximum concentrations set at the detection limit for our EPMA analyses. Also
770 shown are the REE patterns for an ultrarefractory cluster of oxides in Ornans inclusion 1105-
771 42 (Davis 1991) and inclusion HIB-11 from Murchison, which consists of perovskite and
772 spinel in a davisite-rich inclusion (Simon et al. 1996). Error bars for literature analyses are
773 not shown.
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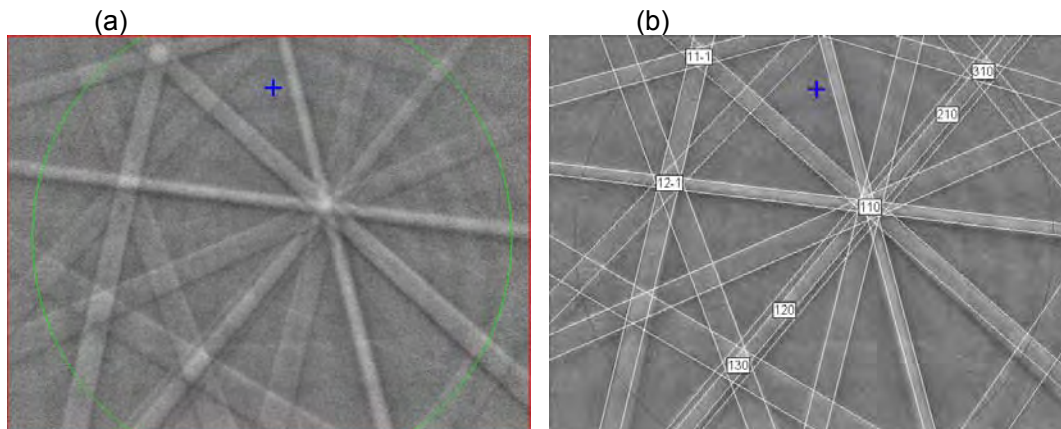
Figure 6. (a) EBSD pattern of the kangite crystal marked with a cross in Figure 2a; (b) the same pattern indexed with the cubic $Ia\overline{3}$ structure obtained by synchrotron micro-diffraction.
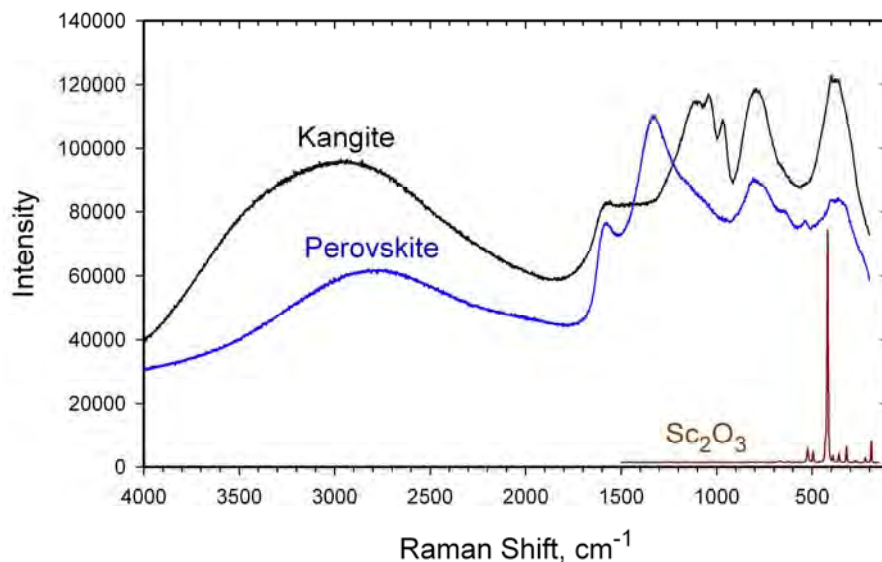
Figure 7. Raman spectra of kangite and perovskite in ACM-3, and synthetic Sc_2O_3. The peaks for kangite and perovskite are dominated by optical fluorescence features due to high concentrations of REEs in the crystals so that no Raman shifts can be distinguished.

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