Supporting Information for:

Revealing the Structures and Relationships of Ca(II)-Fe(III)-AsO_4 Minerals: Arseniosiderite and Yukonite

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Key Words: Yukonite, Arseniosiderite, Pair Distribution Function, TEM, Arsenic

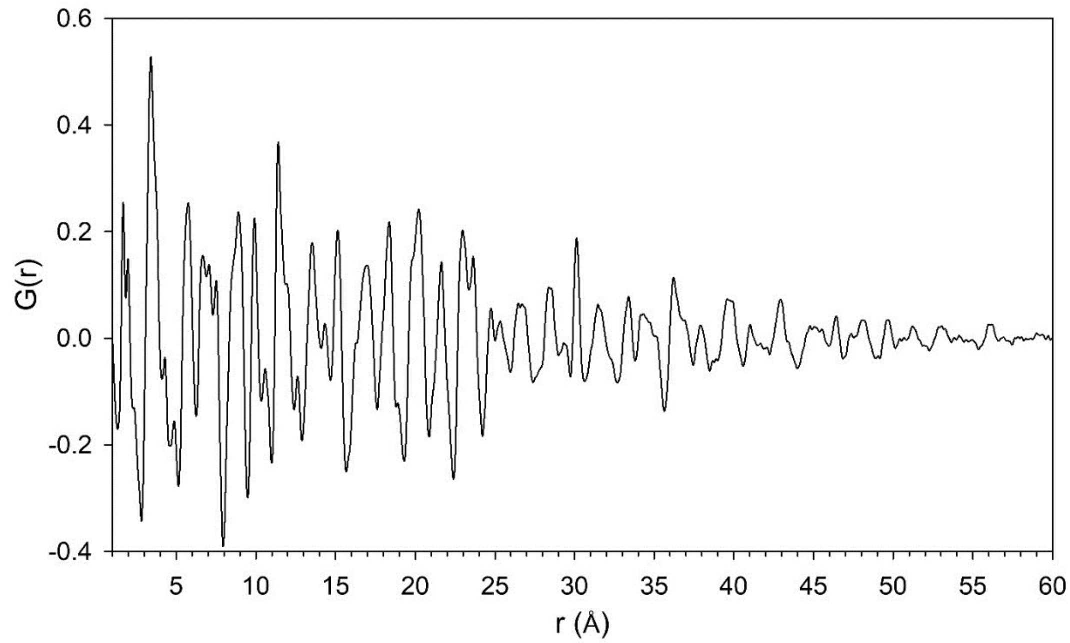

Figure S1. The pair distribution function of the Syn-arseniosiderite produced from total scattering data using 115 keV photons.

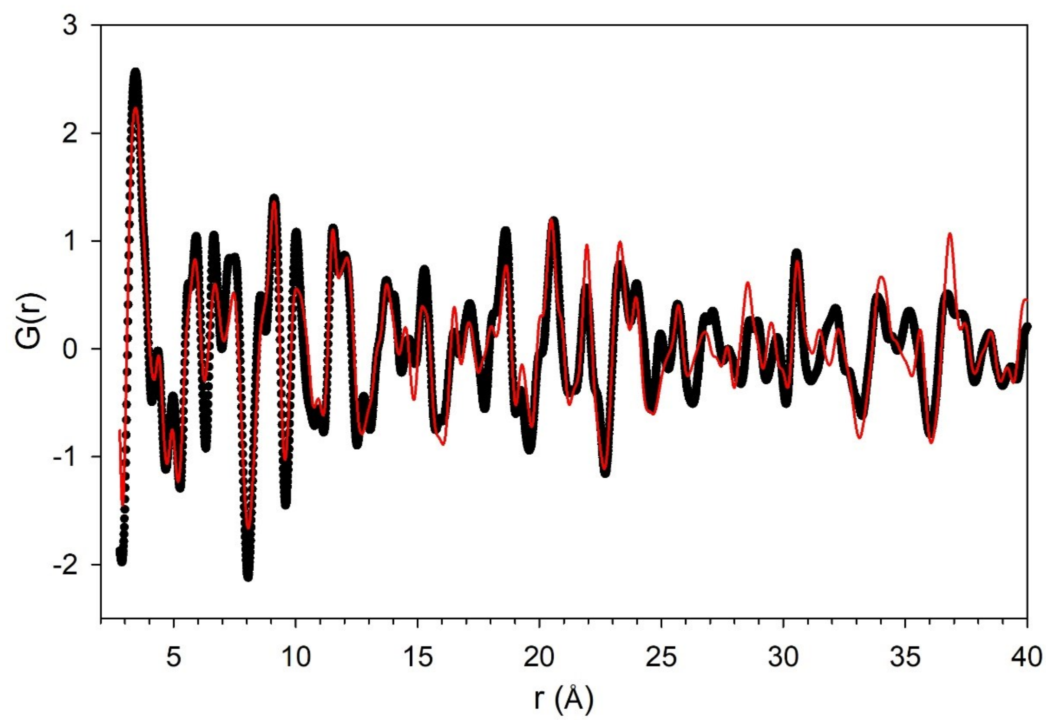

Figure S2. Fit of the LNH arseniosiderite PDF using the mitridatite structure as a model with PDFgui. The unit cell and displacement parameters were refined but not the atomic positions.

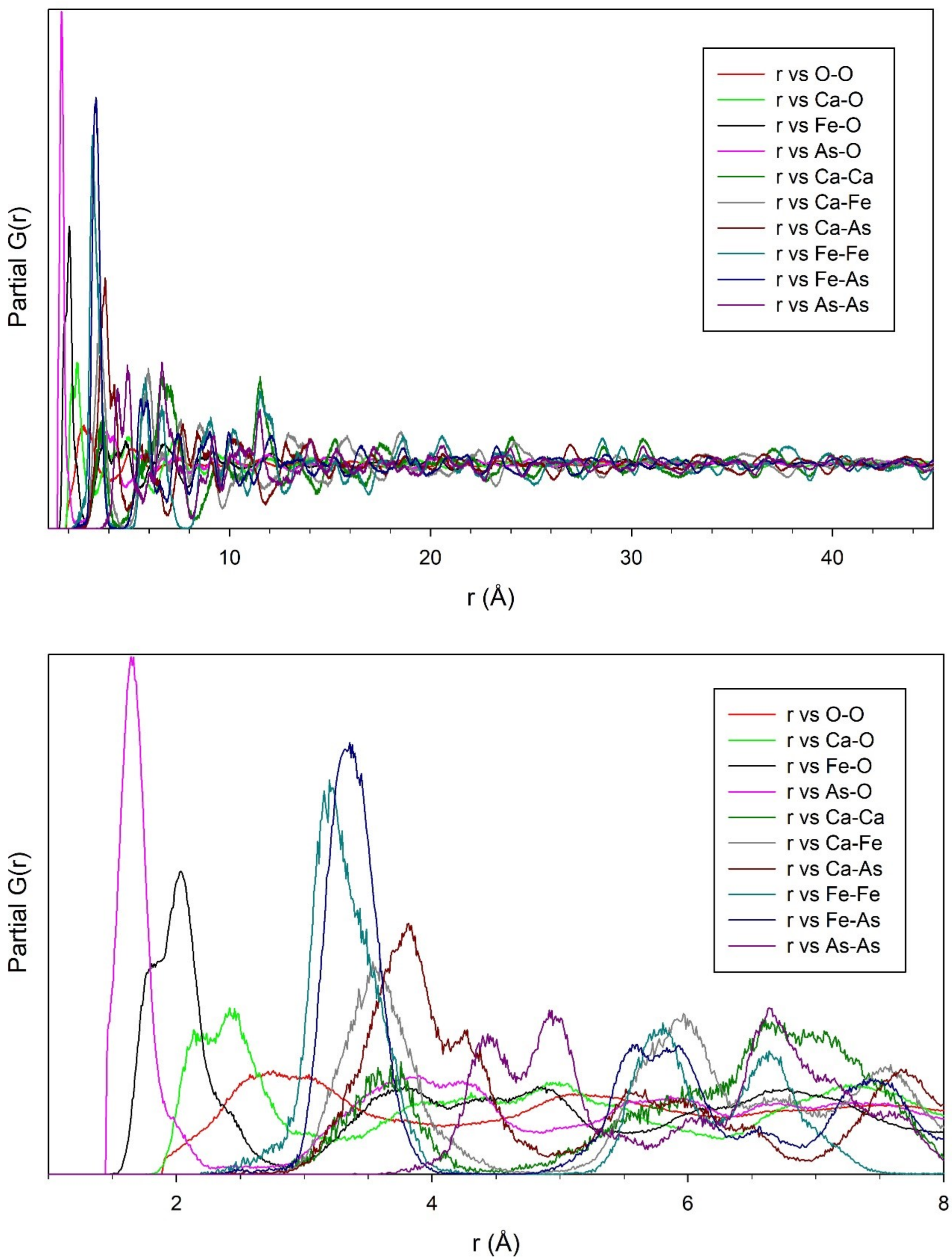

Figure S3. The partial pair distributions functions of the natural LNH arseniosiderite sample obtained from reverse Monte Carlo modeling. Four final configurations were averaged to obtain smoother curves. Top is the full range refined and bottom is a magnification of the low-*r* region.

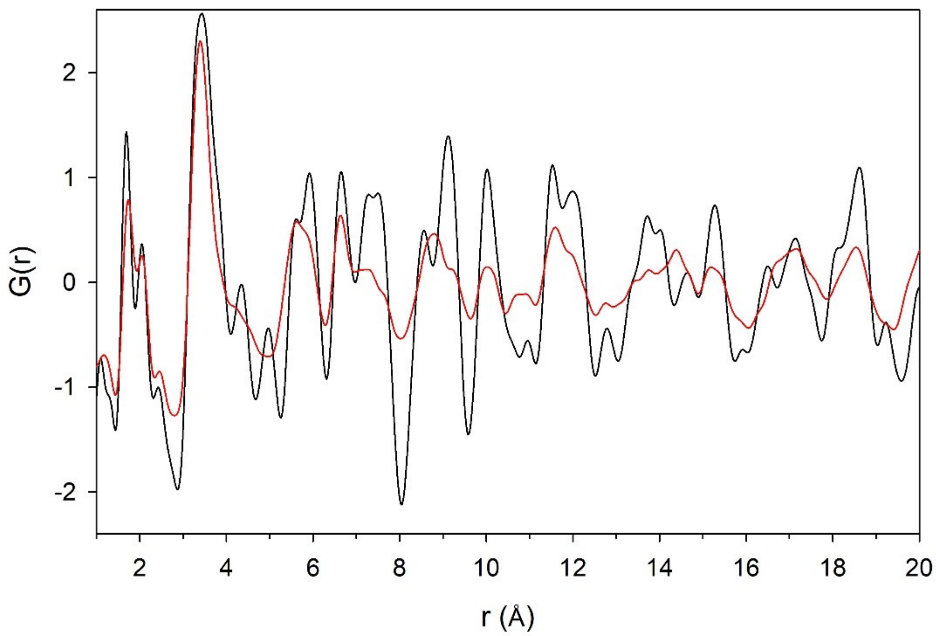

Figure S4. Comparison of the PDFs of the LNH arseniosiderite sample (Ref. # BM 68062; black line) and the LNH yukonite (Ref. # BM.1924, 972; red line).

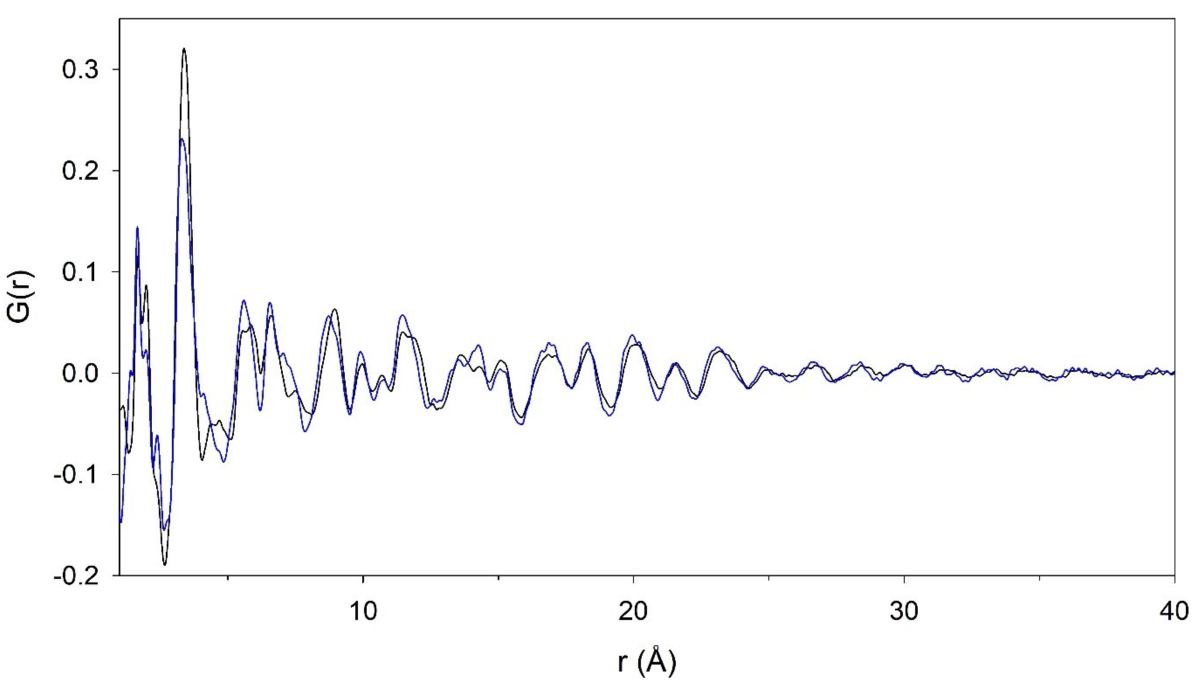

Figure S5. The pair distribution functions of yukonite produced from total scattering data using 115 keV photons. The black curve is the Syn-yukonite and the blue curve is the NMCC sample.

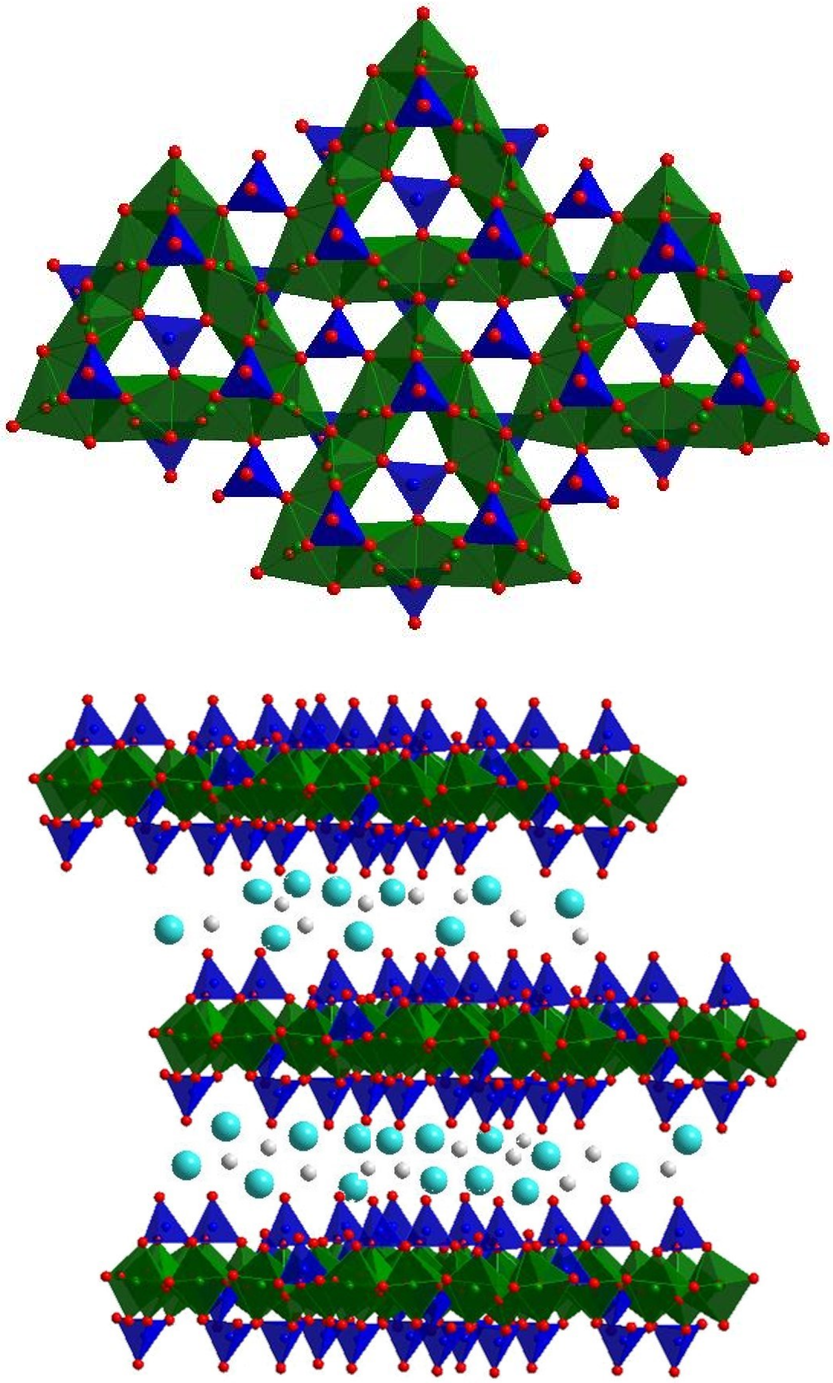

Figure S6. Representations of the structure of yukonite. Green is Fe, blue is As, gray is Ca, red is O, and aqua are water molecules. The top figure shows a layer which is 2×2 nonamers in width. Notice how the small size cause the AsO_4 to FeO_6 ratio to be below 1. The bottom figure shows three such layers loosely connected by Ca^{2+} and H_2O.

Table 1. Overview of proposed chemical formulae of yukonite.

Formula	[Reference(s)]
$2Ca_3As_2O_8 \bullet 3Fe_2As_2O_8 \bullet 5Fe_2(OH)_6 \bullet 23H_2O$	[45]
$(Ca_{6.44}K_{0.13}Mg_{0.23})(Fe_{14.68}Al_{0.36})(AsO_4)_9O_{15.78} \bullet 25.5H_2O$ $(Ca_{5.80}K_{0.11}Mg_{0.27})(Fe_{10.61}Al_{0.52})(AsO_4)_9O_{9.34} \bullet 24.3H_2O$	[12]
$Ca_{6.10}Fe_{13.28}(AsO_4)_{9.20}(OH)_{23.16} \bullet 6.77H_2O$ $Ca_{5.62}Fe_{10.94}(AsO_4)_{8.47}(OH)_{20.34} \bullet 22.99H_2O$ $Ca_{5.12}Fe_{9.96}(AsO_4)_{9.59}(OH)_{16.86} \bullet 10.73H_2O$ $Ca_{6.44}Fe_{11.78}(AsO_4)_{10.00}(OH)_{20.56} \bullet 17.06H_2O$ $Ca_{6.46}Fe_{10.70}(AsO_4)_{9.75}(OH)_{16.37} \bullet 15.72H_2O$	[13]
$Ca_2Fe_3(AsO_4)_3(OH)_4 \bullet 4H_2O$	[16, 34]
$Ca_2Fe_5(AsO_4)_3(OH)_{10} \bullet 2H_2O$ $Ca_2Fe_3(AsO_4)_3(OH)_4 \bullet 5H_2O$ $Ca_2Fe_5(AsO_4)_3(OH)_{10} \bullet 5H_2O$ $Ca_2Fe_3(AsO_4)_3(OH)_4 \bullet 11H_2O$ $Ca_2Fe_5(AsO_4)_3(OH)_{10} \bullet 2H_2O$	[4]
$Ca_{1.76}Fe^{2+}{}_{0.09}Fe^{3+}{}_{3.12}[(As_{0.81}Si_{0.10}P_{0.09})O_4]_3(OH)_{3.76} \bullet 4H_2O$ $Ca_{1.76}Fe^{2+}{}_{0.10}Fe^{3+}{}_{3.56}[(As_{0.89}Si_{0.08}P_{0.03})O_4]_3(OH)_{5.16} \bullet 4H_2O$	[5]
$Ca_3Fe_7(AsO_4)_6(OH)_9 \bullet 18H_2O$ $Ca_{6.5}Fe_{15}(AsO_4)_9O_{16} \bullet 25.5H_2O$	ICDD-PDF35-553 ICDD-PDF51-1416
$Ca_6Fe_{16}(AsO_4)_{10}(OH)_{30} \bullet 23H_2O$	[8]

Table 2. Overview of proposed chemical formulae of arseniosiderite.

Formula	[Reference(s)] and comment
$Ca_2Fe_3(AsO_4)_3O_2\cdot3H_2O$	[1, 2, 4-6, 14, 22, 46] and Nominal composition. However it should be noted that no peroxo O_2 units exist in arseniosiderite as demonstrated via vibrational spectroscopy
$Ca_6Fe_9(AsO_4)_9O_2\cdot9H_2O$	[38]
$Ca_2Fe_3(AsO_4)_3O_2\cdot2H_2O$	[4]
$Ca_3Fe_5(AsO_4)_4(OH)_9\cdot8H_2O$ or $Ca_2Fe_3(AsO_4)_{2.5}(OH)_{5.7}\cdot4.8H_2O$	[4] [28] re-calculated by these authors
$Ca_3Fe_4(AsO_4)_4(OH)_6\cdot3H_2O$	[20, 21, 34]
$Ca_6[Fe_3Fe_6O_6\ (AsO_4)\ (AsO_4)_2\ (AsO_4)_6](OH)_9\cdot9H_2O$	[38] written to show the distinct crystallographic sites
$Ca_{1.9}Fe_3(AsO_4)_{2.7}(SiO_4)_{0.1}(OH)_{4.2}\cdot4H_2O$	[28] re-calculated by these authors based on data presented by [22]
$Ca_2Fe_3(AsO_4)_{2.4}(SiO_4)_{0.5}(OH)_{3.9}\cdot3.3H_2O$ $Ca_{1.9}Fe_3(AsO_4)_{2.7}(SiO_4)_{0.1}(OH)_{4.2}\cdot4H_2O$ $Ca_{1.9}Fe_3(AsO_4)_{2.8}(SiO_4)_{0.1}(OH)_{4.1}\cdot2.4H_2O$ $Ca_{1.5}Fe_3(AsO_4)_{2.3}(SiO_4)_{0.7}(OH)_{3.3}\cdot6.7H_2O$ $Ca_{1.8}Fe_3(AsO_4)_{2.9}(SiO_4)_{0.1}(OH)_{4.6}\cdot2.4H_2O$ $Ca_2Fe_3(AsO_4)_{2.7}(SiO_4)_{0.1}(OH)_x\cdot YH_2O$ $Ca_{0.663}Fe_{1.093}(AsO_4)(OH)_{1.605}\cdot0.827H_2O$	[28] average composition for all synthetic samples [28] average composition for 42 grains of the ketza river study [2] [28] synthetic sample made @ pH 4.5 [28] synthetic samples made @ pH 6-7 [28] EMPA of L3,L4 pores lining samples of ketza river transition sulphide/oxide zone [28] used for thermodynamic calculations and normalized to As.