Santafeite, a re-examination and new empirical formula

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ABSTRACT. Santafeite, known only from New Mexico, USA, is re-examined using single-crystal X-ray and microprobe techniques. The new idealized formula, consistent with space group requirements, is

$$(Mn^{2+},Fe^{3+},Al,Mg)_8(Mn^{4+},Mn^{2+})_8$$
$$(Ca,Sr,Na)_{12}[(VO_4),(AsO_4)]_{16}(OH)_{20} \cdot 8H_2O.$$
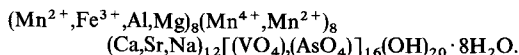
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SANTAFEITE was originally described by Sun and Weber (1958) as a new complex manganese vanadate from the Grants uranium district, McKinley County, New Mexico. Our attention was drawn to this mineral because the original analysis had a low sum (96.2 wt. %), suggesting a possible error, and because the numbers of atoms per cell required by the previously proposed formula, $Na_2O \cdot 3MnO_2 \cdot 6(Mn,Ca,Sr)O \cdot 3(V,As)_2O_5 \cdot 8H_2O$, are inconsistent with the equipoint rank requirements for space group $B22_12$. Two samples of santafeite, one of type material (NMNH 115882) and one deposited in the Smithsonian collection by Ming-Shan Sun (NMNH 112946), were studied. X-ray powder diffraction and microprobe examination showed them to be identical, within error of measurement, and verified their identity as santafeite. Using type material, we have re-examined this mineral using both single-crystal crystallographic methods to verify the space group and microprobe chemical analyses to check the chemical composition.

X-ray crystallography. Weissenberg and precession photographs confirmed the unit cell and space group given by Sun and Weber (1958) ($a = 9.25$, $b = 30.00$, $c = 6.33$ Å; $B22_12$). Sun and Weber also noted that a- and c-axis rotating-crystal photographs have reflections all of which are sharp, but that the b-axis rotation photograph has some diffuse reflections. They noted that 101, 301, 103,

and 303 are diffuse and that this results from 'layer displacements of santafeite in the ac plane'. We observed, however, that for c-axis rotation photographs, all reflections having l odd are diffuse. Weissenberg photographs show that reflections are diffuse parallel to b. This more complete relation is compatible with the diffuseness reported by Sun and Weber. However, it implies only that all layers are identical with respect to the B-centering translation but differ in some as yet undefined way with respect to a and c. Such differences may indeed relate to disorder in a stacking sequence as noted by Sun and Weber, wherein the layers are effectively identical in structure and chemistry but have common substructure elements. However they may also relate to differences between layers in structure and therefore in chemistry. As such, the disorder may reflect local deviations from the ideal structure formula, and in that case may be a reflection of complexities in the formula, as discussed below.

Chemical composition. The two samples of santafeite were analysed using microprobe techniques. Operating conditions were 15 kV and a 0.025 μA sample current. Standards used were synthetic V_2O_3 (V), manganite (Mn), celestine (Sr), synthetic olivenite (As), and hornblende for all other elements. A microprobe scan indicated the absence of elements with atomic number greater than eight, in amounts greater than 0.3 wt. %, other than those reported herein. The data were corrected using a modified version of the MAGIC-4 computer program. The resultant analysis is presented in Table I, together with the original analysis, which is remarkably similar except for some previously undetected Al and Mg, and a lower sum of (SrO, Na_2O,CaO) relative to the new data. Because the analyses are similar in other respects, and because the difference in weights percent oxides for the

	Sun and Weber (1958)	present study
Al_2O_3	n.g.	1.1
Fe_2O_3	0.9	1.1
MgO	n.g.	0.9
CaO	6.2	5.2
SrO	6.0	8.5
Na_2O	4.1	5.0
V_2O_5	35.6	36.5
As_2O_5	2.2	3.2
MnO_2	16.6	16.5§§
MnO	13.7	13.3§§
H_2O	8.8	8.8**
Total	96.2*	100.1

* - includes K_2O < 0.1, CoO 0.1, NiO 0.1, UO_3 0.3,

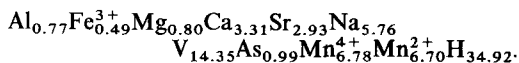   insol. + SiO_2 0.8, CO_2 0.3, CuO 0.5%

** - H_2O from original analysis.

§§ - Oxidation state and ratios of Mn calculated from
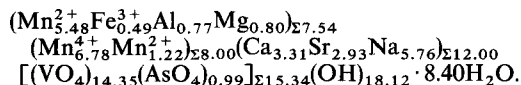
   the original analysis.

n.g. - not given.

aforementioned elements would bring the sum of the previous analysis to an acceptable 100.8%, we have used the H_2O determination of Sun and Weber (1958), noting that with this 8.8% H_2O, our analysis sums to 100.1 wt. %. In the course of our microprobe analyses, we detected substantial variance in the Ca and Sr contents of different crystals. This variance is CaO 5.1-8.5 wt. %; SrO 4.2-8.8 wt. %. The variation is similar for both specimens. Because crystals with high SrO values were more homogeneous, we have reported the composition of these crystals in Table I. These two elements apparently substitute freely for one another because as the proportion of one increases, that of the other decreases. However, the quantity of Na, together with the amounts of the other components, is nearly constant.

Calculation of unit cell contents, using the unit cell parameters and density of Sun and Weber (1958), and the new chemical analysis, yields:

$$Al_{0.77}Fe^{3+}_{0.49}Mg_{0.80}Ca_{3.31}Sr_{2.93}Na_{5.76}$$
$$V_{14.35}As_{0.99}Mn^{4+}_{6.78}Mn^{2+}_{6.70}H_{34.92}.$$

Because we were unable to replicate the analyses for the oxidation state of Mn, we have adopted here the $Mn^{4+}:Mn^{2+}$ ratio of Sun and Weber (1958), who

provided extremely detailed statements concerning their analytical procedures. This presumption, however, introduces ambiguities in writing an idealized formula, as discussed below. Because space group $B22_12$ has equipoint ranks of only 4 and 8, we are constrained by these limitations in drafting an empirical formula. We note for the record, however, that the sum of $(Al+Fe^{3+}+Mg)$ is 2.06 atoms per unit cell, and that Na, shown to be invariant (relative to the pervasive Sr/Ca solid solution) approximates 6 atoms per unit cell. Although Na may be ordered in an equipoint of rank 4, and Sr, Ca, and excess Na may be ordered on one of rank 8, this is conjecture and we have here grouped them together. Therefore, there may be fine details of the crystal structure of santafeite, as yet undetermined, which may permit some ordering of these components. The above unit cell contents yield the formula:

$$(Mn^{2+}_{5.48}Fe^{3+}_{0.49}Al_{0.77}Mg_{0.80})_{\Sigma7.54}$$
$$(Mn^{4+}_{6.78}Mn^{2+}_{1.22})_{\Sigma8.00}(Ca_{3.31}Sr_{2.93}Na_{5.76})_{\Sigma12.00}$$
$$[(VO_4)_{14.35}(AsO_4)_{0.99}]_{\Sigma15.34}(OH)_{18.12}\cdot8.40H_2O.$$

Charge balance for this formula requires 88 oxygens per se; however, the quantities of some constituents are apparently low in sum (V,As,Mn^{2+}), and an idealized formula requires 92 oxygen atoms:

$$(Mn^{2+},Fe^{3+},Al,Mg)_8(Mn^{4+}Mn^{2+})_8(Ca,Sr,Na)_{12}$$
$$[(VO_4),(AsO_4)]_{16}(OH)_{20}\cdot8H_2O.$$
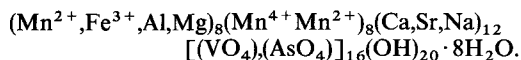
In addition, until a crystal structure analysis is performed, the true oxidation state of Mn in santafeite remains ambiguous. Accordingly, we wish to treat the above given $(OH)_{20}$ as $(OH,O)_{20}$ to accommodate this ambiguity. Lastly, the X-ray diffraction data showed that there is significant disorder in the structure. In so far as this disorder relates to local variation from an ideal structure, the formula may deviate from an apparently ideal one. For example, the apparent substitution of As for V, and the fact that they sum to a value (15.34) significantly different than that required for the ideal space group (16) may be related to that disorder. Considering all of these relations, the idealized formula can be written as

$$(Mn,Fe^{3+},Al,Mg)_8Mn^{4+}_8(Ca,Sr,Na)_{12}$$
$$(VO_4)_{16}(OH,O)_{20}\cdot8H_2O.$$
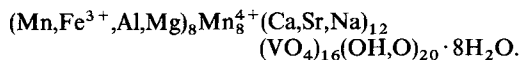
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