MARICOPAITE, A NEW HYDRATED Ca–Pb, ZEOLITE-LIKE SILICATE FROM ARIZONA

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ABSTRACT

Maricopaite is a new mineral from the Moon Anchor mine, near Tonopah, Maricopa County, Arizona, occurring as sprays of translucent white, acicular crystals with mimetite. The unit-cell contents suggest that the formula is (Pb_7Ca_2) $(Si, Al)_{48}O_{100} \cdot 32H_2O$, implying a structure having a high degree of polymerization approaching that of a tectosilicate. Maricopaite is orthorhombic, space group $Cmmm$, $C2mm$, $Cmm2$ or $C222$, with a 19.65 (2), b 19.40(3) and c 7.531(7) Å. The principal lines in the X-ray powder diffraction are $[d(Å),I,hkl]$: 13.7(100) (110), 9.86(40) (200), 3.357(40) (530), 3.216(50) (312), 2.978(40) (402,042,061), 2.845(40) (422,242,261). Maricopaite is soft and friable and has an imperfect {010} cleavage; D_{meas} 2.94 g/cm³, D_{calc} 2.96 g/cm³. Optical properties include: α 1.563(3), β 1.582(3), γ 1.592 (calc.), $2V$ 70(10)°, $X = a$, $Y = c$, $Z = b$; $r>v$. Infrared data, the form of the water loss, the low density, and the similarity of chemical and crystallographic data to those of mordenite imply that maricopaite may be a zeolite.

Keywords: maricopaite, silicate, new mineral, Arizona.

SOMMAIRE

La maricopaïte, nouvelle espèce minérale, a été découverte dans la mine de Moon Anchor, près de Tonopah, comté de Maricopa, en Arizona; on la trouve en rosettes de cristaux blancs translucides avec la mimetite. Selon le contenu de la maille élémentaire, la formule serait (Pb_7Ca_2) $(Si, Al)_{48}O_{100} \cdot 32H_2O$, ce qui implique un degré élevé de polymérisation, comme dans une tectosilicate. La maricopaïte est orthorhombique, groupe spatial $Cmmm$, $C2mm$, $Cmm2$ ou $C222$, avec a 19.65(2), b 19.40(3), c 7.531(7) Å. Les six raies les plus intenses du cliché de poudre $[d$ en Å$(I)(hkl)]$ sont: 13.7(100) (110), 9.86(40) (200), 3.357(40) (530), 3.216(50) (312), 2.978(40) (402,042,061), 2.845(40) (422,242,261). C'est un minéral mou et cassant qui possède un clivage {010} imparfait; sa densité est de 2.94 (mesurée) ou 2.96 (calculée). Propriétés optiques: α 1.563(3), β 1.582(3), γ 1.592 (calculé), $2V$ 70(10)°, $X = a$, $Y = c$, $Z = b$; $r >v$. D'après les données d'absorption infra-rouge, l'allure de la perte en eau, la faible densité, et la ressemblance des données chimiques et cristallographiques à celles de la mordenite, la maricopaïte pourrait être une zéolite.

(Traduit par la Rédaction)

Mots-clés: maricopaïte, silicate, nouvelle espèce minérale, Arizona.

INTRODUCTION

In late 1983, Mr. William Hunt of Sun City, Arizona, called an unidentified mineral to our attention. It had been found near Tonopah, Arizona, and he thought that it might be a new species. Our study has shown this to be the case, and the description of this new mineral species is presented here. We have named this mineral *maricopaite* for the county in Arizona where it was found. The species and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved in the Smithsonian Institution under catalog numbers NMNH 163248 and 163247.

OCCURRENCE

Maricopaite is known from only one locality, 1 Moon Anchor mine, approximately 15 km west of Tonopah, Maricopa County, Arizona. We quote

here from the notes of Mr. Hunt, who found the material: "The specimens came from the hanging wall of the vein which consists of calcite–fluorite gangue with many square voids (presumably due to dissolution of galena). The secondary minerals I have seen are cerussite, mimetite, fornacite, phoenicochroite, duftite, chrysocolla, and wickenburgite." The assemblage that makes up the type specimens is rather simple, consisting of maricopaite associated with sprays of orange mimetite on a quartz matrix. Maricopaite, together with mimetite that apparently formed at approximately the same time, coats and fills fractures in the quartz. Most maricopaite occurs as thin bundles of extremely elongate acicular crystals, frequently as mats with admixed mimetite. Radial sprays up to 1.0 mm in diameter are common.

X-Ray Crystallography

A prismatic crystal was mounted along the direction of elongation [001] and studied by Weissenberg ($CuK\alpha$) and precession methods ($CuK\alpha$ and $MoK\alpha$). $CuK\alpha$ radiation was used for most of the precession photographs to ensure resolution of the closely spaced levels resulting from the large a and b dimensions. Extinctions are consistent with space groups $Cmmm$, $C2mm$, $Cmm2$ or $C222$. Cell parameters originally determined from single-crystal photographs were refined by least squares, utilizing data from a Gandolfi powder-diffraction pattern, yielding the values a 19.65(2), b 19.40(3) and c 7.513(7)
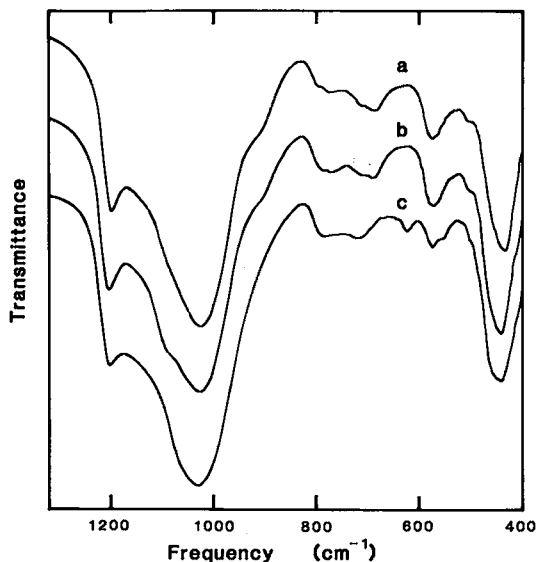

Fig. 1. Infrared spectra of maricopaite: (a) unheated, (b) heated at 110°C in air for 15 hours under vacuum of 2 mm Hg, (c) heated at 400°C for 16 hours in air.

Å, V 2864(4) Å^3. The powder-diffraction data listed in Table 1 were obtained using a Gandolfi camera with 114.6 mm diameter, $FeK\alpha$, Mn-filtered radiation, a Si internal standard, and a polycrystalline specimen.

The crystallographic data are similar to those of the zeolite mordenite, which has a 18.1, b 20.5 and c 7.5 Å, space group $Cmcm$ (Gottardi & Galli 1985). Because maricopaite has a composition having zeolite-like affinities, as discussed below, the similarities in cell parameters may reflect common structural units.

Physical and Optical Properties

Maricopaite is generally white and translucent, but small crystals may be colorless and transparent. The luster is silky to vitreous. There is no discernible fluorescence under ultraviolet radiation or under the beam of the electron microprobe. Hardness was not directly determined as the crystals are too small, but maricopaite was observed to be extremely soft and friable. The cleavage is imperfect, {010}. The density is 2.94 g/cm^3, measured with heavy liquids, compared with a calculated value of 2.96 g/cm^3.

Optically, maricopaite samples consist of radiating fibers that are intimately intergrown and display complex extinction effects. Even small grains on the order of 20–30 μm in size display patchy and undulose extinction. Consequently, the optical measurements could be made on only the few very small grains which were optically uniform. This, combined with the preferred orientation due to the {010} cleavage, prevented direct measurement of all optical parameters; e.g., no BXa figures could be observed as γ is perpendicular to the cleavage and γ could not be directly measured. Thus $2V$ as measured from BXo figures is relatively inaccurate, and the value for γ is calculated from other parameters. Maricopaite is biaxial negative, with $2V = 70(10)°$, and indices of refraction α 1.563(3), β 1.582(3), and γ 1.592 (calc.). The orientation is $X = a$, $Y = c$, and $Z = b$. There is strong dispersion with $r > v$.

Chemical Composition

Maricopaite was chemically analyzed using an ARL-SEMQ electron microprobe operated under the following conditions: 15 kV, sample current 0.025 μA measured on brass, broad beam to minimize H$_2$O volatilization, and standards PbO (Pb) and hornblende (Ca, Al, Si). A wavelength scan was carried out to check for the presence of elements other than those reported, but none was observed. The wavelength-dispersive data were corrected using a modified version of the MAGIC-4 program.

Water and other volatiles were determined using

a Mettler TAl thermoanalyzer for TGA data, with identification of evolved species (EGA) determined by an Inficon IQ 100 quadrupole mass spectrometer. The specimen presented analytical problems in that it was difficult to obtain a reasonable amount of the pure sample for analysis. Ultimately, two samples were prepared.

The first was carefully hand-separated and crushed in acetone, but still contained an estimated 5–10% impurities, presumably mimetite and quartz. This was used for the first thermal analytical run. The second sample was purified by centrifuging in a methylene iodine – acetone density gradient. This produced a sample free from impurities at optical resolution. A portion of the second sample was used for the infrared study and the remaining 565 micrograms were used for a second thermal analytical run. The results from both analyses have been used to produce the final weight-loss values. The first run was with a reasonable sample size (2.54 mg), but the sample contained minor impurities. The second run was with a pure sample, but the sample was too small (0.565 mg) for the most accurate measurements.

Following weighing at 40% relative humidity the sample as contained in a Pt crucible was placed at a high vacuum of 2×10^{-8} torr in the thermoanalyzer at 20°C for 3.5 hours. During this time it lost 6.5 wt.%, assumed to be in the form of H_2O. The sample was then heated at a rate of 10°C/min., and lost 4.5 wt.% H_2O continuously from 50 to 500°C, with a peak at approximately 100°C. The water loss was typical of those observed from zeolites. In the first run a loss of hydrogen was detected between 250 and 400°C, with a peak of 360°C. In the second run this 0.5 wt.% loss was identified as being due to the breakdown of hydrocarbons. Further loss occurred above 500°C and corresponded to fusing of the sample. The total weight loss due to water was 11.0 wt.%, and that due to hydrocarbons was 0.5 wt.%.

The major-element analyses give rise to the values SiO_2 42.0, Al_2O_3 11.4, CaO 2.4, PbO 30.8, H_2O 11.0, hydrocarbon 0.5, total 98.1 wt.%, from which the unit-cell contents were calculated using the observed density and lattice parameters to give the empirical formula:

$Pb_{7.00}Ca_{2.17}(Si_{35.46}Al_{11.34})_{46.80}O_{97.10} \cdot 30.96H_2O$ + minor hydrocarbon.

The interpretation of the loss of hydrogen as being due to breakdown of organic compounds is compatible with the presence in the structure of large zeolite-like cavities (see below). Kotasthane & Shiralkar (1986) found that pure tetraalkyl ammonia compounds decomposed in the temperature range 250–270°C, but when contained in the channels of a synthetic zeolite, the decomposition temperature was increased to 350 to 500°C. The observed temperature range for loss of hydrogen is thus a reasona-

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR MARICOPAITE.

I/I_0 [1]	d(Obs)	d(Calc) [2]	hkl	I/I_0	d(Obs)
100	13.7+	13.8	110	20	2.456
40	9.86+	9.83	200	1	2.424
10	6.92+	6.90	220	2	2.388
5	6.58+	6.60	111	5	2.223
5	6.21+	6.21	310	2	2.180
2	6.01	5.97	201	1	2.141
20	4.79+	4.79	311	1	1.976
30	4.35+	4.35	240	2	1.949
5	4.12+	4.11	401	5	1.885
2	3.626+	3.625	112	2	1.866
10	3.513+	3.509	202	1	1.846
		3.503	012	2	1.793
5	3.448+	3.451	440	1	1.758
40	3.357	3.359	530	2	1.694
10	3.289	3.300	222	5	1.619
		3.276	600	5	1.556
50	3.216+	3.214	312	2	1.524
2	3.135	3.136	441	2	1.470
20	3.056	3.066	531	2	1.416
		3.050	351	5	1.292
40	2.978	2.984	402	2	1.272
		2.970	042		
		2.969	061		
40	2.845	2.852	422		
		2.843	242		
		2.842	2.61		
20	2.687+	2.690	512		
20	2.552	2.553	641		
		2.552	370		

[1] Intensities visually estimated.
[2] d-values calculated with lattice parameters
$\underline{a} = 19.655$, $\underline{b} = 19.395$, $\underline{c} = 7.513$ Å.
+ Reflections used in least-squares refinement.

ble one for breakdown of hydrogen-containing molecules. Calculations of the Gladstone–Dale relationship using the constants of Mandarino (1981), the chemical data listed above, and the measured indices of refraction and density, yield a compatibility index $(1-K_P/K_C)$ of 0.054, indicating good compatibility of the data (Mandarino 1979).

INFRARED ANALYSIS

High-resolution (2.0 cm⁻¹) infrared spectra in the region 400–4000 cm⁻¹ were recorded using a Nicolet Fourier transform interferometric infrared spectrophotometer. Three samples were run corresponding to the conditions: (1) no pre-treatment of sample, (2) sample heated for 15 hours at 110°C under vacuum, (3) sample heated again at 400°C for the 16 hours in air. The sample chamber was purged with dry nitrogen before and during spectrum measurement, except for sample (3), the spectrum of which was recorded at ambient room atmosphere. Frequency measurements were calibrated internally against a He/Ne laser and are accurate to ±0.01 cm⁻¹. Spectra for the region 400 to 1300 cm⁻¹ are shown in Figure 1.

The portion of the spectrum that is characteristic of H_2O is not shown, but it displayed intense

absorptions at 1637, 3220 and 3435 cm^{-1} for the untreated sample. The intensity of these peaks decreased by approximately 50% for the sample heated at 110°C, and nearly 100% after heating at 400°C.

The portion of the spectra displaying lattice vibrations (Fig. 1) has numerous peaks that correlate with the internal and external asymmetric vibrations of the (Si, Al)O_4 tetrahedra common to all zeolites and other tectosilicates (900–1300 cm^{-1}). The next most intense group (443 cm^{-1}) corresponds to the internal vibrations of (Si,Al)O_4 tetrahedra, and is also common to zeolites. The less intense peaks between these two groups are due to the internal and external symmetric vibrations of tetrahedra, and to probable ring configurations of various kinds.

The spectrum for the specimen heated at 400°C is similar to the other two except for the region normally attributed to double rings; the single peak of the two lower temperature spectra has been replaced by several peaks that are generally characteristic of single-ring structures. This implies that heating may have caused some rearrangement of the tetrahedra, although this is problematical. This spectrum is virtually identical to one for Zeolon that was also recorded at 400°C (Flanigen 1976). Zeolon is a synthetic zeolite that has the mordenite-type structure.

DISCUSSION

The very high water content and the resemblance of the form of the water loss and the infrared spectra to those of zeolites suggest that the structure of maricopaite contains large cage-like voids similar to those found in zeolites and related structures. The low measured density (2.94 g/cm^3) is consistent with such an open structure, especially when the presence of significant Pb is considered. This suggests that at least a significant fraction of the Al must be tetrahedrally coordinated. Assuming that all Al is in tetrahedral coordination gives rise to the O: (Si + Al) ratio of 97.1:46.8, which is just slightly greater than the value of 2 found in tectosilicates. It is therefore tempting to conclude that maricopaite is a zeolite, especially when the similarity of its unit-cell parameters and infrared spectrum with those of mordenite is considered. In addition, the O: (Si + Al) ratio for one unit cell of mordenite is 96:48, very similar to that of maricopaite.

A zeolite-type structure would require that both Pb and Ca occupy large voids, creating an unusual role for Pb. The amounts of these two divalent cations are simply too large for charge balance of a Si/Al framework, even considering larger than reasonable errors of analysis. The value of 7.00 Pb atoms per cell is inconsistent with the ranks of all equipoints of the possible space groups, which must be multiples of two. However, the number of cations occupying voids in zeolites commonly varies with fractional occupancy of equipoints. The Pb content may thus actually be consistent with such a structural relation. Three-dimensional intensity data have been measured in order to solve the crystal structure. Analysis of the Patterson function shows that heavy atoms occupy two equipoints of rank 4 in space group $Cmm2$. These results are only tentative, however.

The above relations are generally consistent with a structure having a high proportion of shared vertices of Si and Al tetrahedra, approaching that of a tectosilicate. Such structures occur, for example, in the reyerite family (Gard et al. 1975, Dunn et al. 1984) where double sheets may accommodate large cations and H_2O. In addition, jagoite has a structure closely related to that of members of the reyerite group, but has 3-coordinated Pb contributing to the polyhedral framework (Mellini & Merlino 1981). Such a relation cannot be discounted for maricopaite.

Given all of these relations, our best estimate for the formula of maricopaite is (Pb$_7$Ca$_2$)(Si, Al)$_{48}$O$_{100}$ ·32H$_2$O ($Z = 1$) where the total of Ca and Pb may vary, as is true of alkalis and the alkaline-earth cations in zeolites, and the ratio of oxygen to tetrahedrally coordinated (Si = Al) approaches that of a tectosilicate. The number of water molecules has been set equal to a multiple of the equipoint ranks, but as in zeolites it is probably not constant. The crystal structure has a high proportion of shared vertices and is either that of a zeolite or is zeolite-like. Complete crystal-structure analysis will be necessary in order to define the structure relations and to provide a firm definition of details regarding the chemical formula.

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