

Jaffeite, a new hydrated calcium silicate from the Kombat mine, Namibia*

H. SARP

Departement de minéralogie et pétrographie, Muséum d'Histoire naturelle, Genève, Switzerland

DONALD R. PEACOR

Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

ABSTRACT

Jaffeite, ideally $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$, is the natural analogue of the phase $\text{C}_3\text{SH}_{1.5}(3\text{CaO}\cdot\text{SiO}_2\cdot 1.5\text{H}_2\text{O}$; tricalcium silicate hydrate; TSH) that occurs as a component of cement. It is hexagonal, space group $\text{P}\bar{3}$, with $a = 10.026(5)$, $c = 7.482(4)$ Å, and $Z = 2$. The strongest lines in the X-ray powder-diffraction pattern are [d (Å), I , hkl] 8.66, 100, 010; 3.279, 50, 210; 2.996, 90, 112; 2.887, 70, 030; 2.833, 90, 022; 2.466, 30, 212; 2.083, 30, 222; 1.872, 25, 042, 004; and 1.757, 30, 232. Jaffeite is colorless with a vitreous luster; $D_{\text{meas}} = 2.65(3)$, $D_{\text{calc}} = 2.58(2)$ g/cm³. Optical properties include uniaxial (+); $\omega = 1.596(2)$, $\epsilon = 1.604(2)$. Jaffeite occurs at the Kombat mine, Namibia, in a low-grade metamorphic setting, with major defernite and hausmannite, and minor brucite, hillebrandite, vesuvianite, glaucocroite, apatite, galena, and native copper.

INTRODUCTION

In 1985 Pete J. Dunn sent a sample containing defernite that had been collected at the Kombat mine to one of us (H.S.), in order that a detailed comparison with type defernite from Turkey (Sarp et al., 1980) could be carried out. This study verified that the specimen did indeed consist principally of defernite, leading to a description of its crystal structure, properties, and paragenesis (Peacor et al., 1988). Detailed characterization utilizing petrographic and electron-microprobe analytical techniques revealed the presence of a mineral that could not be matched with any known phase. Subsequent detailed studies have confirmed that it is indeed a new mineral, and we have named it jaffeite in honor of Professor Howard Jaffe of the University of Massachusetts, in recognition of his many contributions to the fields of mineralogy and petrology. The mineral and name were approved prior to publication by the Commission on New Minerals and Minerals Names, IMA. Type material is preserved in the Department of Mineralogy of the Natural History Museum of Geneva under catalogue number 500/32. It is also present in a specimen of defernite under catalogue number NMNH 163802 (Peacor et al., 1988) in the Smithsonian Institution.

X-RAY CRYSTALLOGRAPHY

Single-crystal precession studies showed that jaffeite is hexagonal with space group $\text{P}3$ or $\text{P}\bar{3}$. These and other data verified that jaffeite is the natural analogue of synthetic $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$, for which Kazak et al. (1974) de-

termined that the space group is $\text{P}\bar{3}$ based on a structure determination. The space group of jaffeite is therefore $\text{P}\bar{3}$ by analogy. The unit-cell parameters [$a = 10.026(5)$, $c = 7.482(4)$ Å, $V = 651.34(3)$ Å³] were determined by least-squares refinement of powder-diffraction data (Table 1) as obtained from a 114.6-mm-diameter Gandolfi camera, $\text{CuK}\alpha$ (Ni-filtered) radiation, and a sample consisting of two crystals. The powder-diffraction pattern is virtually identical to that of synthetic $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$, as shown in Table 1.

PHYSICAL AND OPTICAL PROPERTIES

Jaffeite occurs as euhedral to subhedral elongated crystals (average length 0.4 mm) with hexagonal cross sections (average diameter 0.25 mm), always embedded within other minerals such as defernite. The crystals are elongated parallel to [001]; the only forms observed are {001} and {100}. Jaffeite is transparent and colorless with a vitreous luster and a white streak. It is brittle and the fracture is conchoidal. An imperfect {100} cleavage appeared to be present, but because the grains are very small, it was difficult to observe the cleavage and its existence is problematical. Hardness could not be measured because of the small grain size. Density, measured using heavy liquids, is 2.65(3) g/cm³; the calculated value is 2.58(2) g/cm³. Jaffeite is soluble in HCl. Jaffeite is optically uniaxial positive with indices of refraction $\omega = 1.596(2)$, $\epsilon = 1.604(2)$ as determined with light of wavelength 5890 Å.

CHEMICAL COMPOSITION

Jaffeite was chemically analyzed using an ARL EMX-SM electron microprobe operated at a voltage of 15 kV and sample current of 40 nA as measured on benitoite. Qual-

* Contribution no. 458, The Mineralogical Laboratories, Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

TABLE 1. X-ray powder-diffraction data for jaffeite compared with those of synthetic $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$ (JCPDS 29-375)

JCPDS 29-375		Jaffeite			
<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>I</i> / <i>I</i> ₀
010	8.6	95	8.683	8.66	100
110	5.00	25	5.013	4.995	5
020	4.34	2			
012	3.430	10	3.436	3.417	5
210	3.285	70	3.282	3.279	50
112	2.998	85	2.998	2.996*	90
030	2.898	95	2.894	2.887	70
022	2.834	100	2.834	2.833*	90
220	2.508	6			
212	2.468	50	2.467	2.466*	30
310	2.411	8			
131	2.290	2	2.292	2.292	<5
040	2.172	17	2.171	2.174	10
222	2.083	50	2.082	2.083	30
132	2.025	12	2.025	2.028*	5
320	1.993	25	1.992	1.994*	10
410	1.896	2			
042	1.878	35	1.878	1.872	25
004	1.876	40	1.870		
014	1.824	4	1.829	1.820	<5
232	1.759	40	1.758	1.757*	30
142	1.690	30	1.690	1.691*	25
330	1.671	8	1.671	1.675	<5
240	1.642	8	1.641	1.641*	<5
214	1.623	8	1.625	1.627*	<5
034	1.570	25	1.571	1.572*	25

* Reflections used in least-squares analysis.

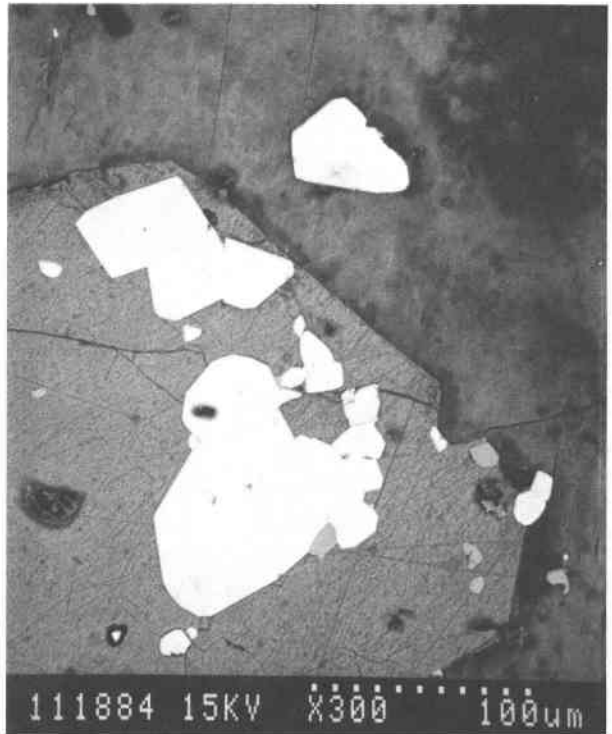


Fig. 1. Backscattered-electron image of a thin section containing jaffeite (lower left, gray, portion of hexagonal cross section), hausmannite (white), defernite (dark gray and mottled, upper and right areas), and apatite (small light gray crystals within jaffeite).

itative analyses showed that the only major elements present having atomic number greater than nine are Ca and Si, although Mn and Cl were shown to be present in trace amounts (<0.1 wt%). Wollastonite was, therefore, used as a standard for quantitative analyses, the results of which are listed in Table 2. The amount of water was calculated by difference as there was not sufficient material for an analysis. These results lead to the empirical formula $\text{Ca}_{5.86}\text{Si}_{2.02}\text{O}_{13}\text{H}_{6.21}$ (based on O = 13), in excellent agreement with the ideal formula of the synthetic analogue, $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$ (Z = 2). In addition, the analytical results give rise to an excellent compatibility index (Mandarino, 1981) with $1 - K_p/K_c = -0.036$, further implying that the calculated water content is accurate.

OCCURRENCE

Jaffeite is only known to occur in the specimen that had been examined in a study of defernite from the Kom-

TABLE 2. Electron-microprobe analytical data (wt% oxides) for jaffeite

	1	2	3	4	5
CaO	65.33	65.32	64.29	64.98	65.88
SiO ₂	23.42	24.16	24.30	23.96	23.53
H ₂ O*	11.25	10.52	11.41	11.06	10.59
	100.00	100.00	100.00	100.00	100.00

Note: column 4, average of analyses 1–3; column 5, weight percentages calculated for the ideal formula $\text{Ca}_6\text{Si}_2\text{O}_7(\text{OH})_6$.

* Calculated by difference.

bat mine, Namibia, for which the detailed occurrence and associations were described by Peacor et al. (1988). In addition, the mineral deposits and geology of the mine have been described by Innes and Chaplin (1986). These relations will, therefore, not be described in detail. However, jaffeite was discovered in thin sections, for which additional petrographic and scanning-electron-microscopy studies were carried out, and those results will be described here.

Jaffeite forms euhedral and subhedral crystals closely associated with and commonly contained within idiomorphic laths of defernite approximately 1 cm in diameter (Fig. 1). The defernite, which makes up the bulk of the specimen studied, is found within a matrix of fine- to medium-grained hausmannite, euhedral crystals of which occur dispersed throughout the defernite (Figs. 1 and 2) and other minerals. In addition, subhedral grains of brucite, hillebrandite (Fig. 2), vesuvianite (pseudo-octahedral in shape and containing a trace of REE), apatite, and glaucocroite were found dispersed throughout the defernite matrix. The outlines of grains of all of these minerals are sharp, with contacts and boundaries typical of metamorphic texture. There is no evidence of replacement or alteration. Given the low-grade metamorphic setting of the deposit as a whole, these relations imply that the minerals apparently formed as an equilibrium assemblage,



Fig. 2. Backscattered-electron image of a thin section containing defernite (gray), hillebrandite (light gray), and hausmanite (white).

but proof of such relations must depend on further petrologic work. Native copper also occurs as thin films along cleavage planes of defernite, and galena is dispersed throughout the sample in uncommon grains a few micrometers in diameter. The apatite contains some Si and S, apparently in substitution for P. The glaucocroite has the approximate composition $\text{Ca}_{1.4}\text{Mn}_{0.6}\text{SiO}_4$, as determined by electron-microprobe analysis. All minerals were identified by utilizing optical, electron-microprobe, and scanning-electron-microscope (SEM) data. The SEM observations were carried out primarily in backscattered-electron mode, with qualitative analyses of individual minerals obtained by energy-dispersive X-ray analysis.

DISCUSSION

$\text{Ca}_3\text{Si}_2\text{O}_7(\text{OH})_6$ is a constituent of cement, where it is known as " $\text{C}_3\text{SH}_{1.5}$ " (hydrated calcium silicate with $\text{CaO}:\text{SiO}_2:\text{H}_2\text{O} = 3:1:1.5$) and "TSH" (tricalcium silicate hydrate). Comparison of the formula, physical properties, X-ray powder-diffraction pattern (Ingram and Taylor, 1987, JCPDS card 29-375), and crystallographic parameters, which were determined as part of a crystal-structure analysis (Kazak et al., 1974), show that the synthetic phase is essentially identical to jaffeite.

Because both jaffeite and hillebrandite occur in the system $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$, their coexistence in an apparent state

of equilibrium is constrained by the phase relations in that system. Those relations were determined by Roy and Harker (1962) under low-pressure hydrothermal conditions and by Roy and Johnson (1967) at high H_2O pressure. Roy and Harker showed that hillebrandite and "TSH" (jaffeite) both form and may coexist at temperatures up to approximately 350 °C. At that temperature, hillebrandite is replaced by calciochondrodite [now known as the mineral reinhardbraunsite (Hamm and Hentschel, 1983)] and fluid. Jaffeite was found to form at temperatures up to approximately 525 °C, where it, too, decomposes to calciochondrodite plus fluid.

On the other hand, Roy and Johnson (1967) showed that hillebrandite and jaffeite can form together between 175 and 235 °C at high $P_{\text{H}_2\text{O}}$, but that calciochondrodite occurs above that temperature, forming either with hillebrandite or jaffeite; the latter two phases are incompatible according to that relation. However, hillebrandite remains stable up to approximately 340 °C and jaffeite to temperatures above 500 °C under high $P_{\text{H}_2\text{O}}$ conditions.

Taylor (1962, 1969) reviewed the formation conditions for phases in the system $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ and emphasized the difficulty of obtaining equilibrium in laboratory syntheses. Roy and Harker (1962) similarly voiced concern that their graphical portrayals of phases might not represent equilibrium states. Taylor (personal communication) has noted that reaction temperatures are therefore generally observed to be too high. He has suggested that the synthesis of calciochondrodite (with jaffeite as the major phase) at a temperature as low as 180 °C (Imlach and Taylor, 1972) might imply that hillebrandite and/or jaffeite are replaced by calciochondrodite at temperatures much less than 350 °C.

It is clear that the syntheses described above may have limited relevance to natural equilibrium assemblages as apparently observed for hillebrandite and jaffeite. However, the experiments are consistent with the general low-temperature metamorphic conditions, suggesting a temperature of formation of less than 350 °C, under hydrous conditions in a system with relatively low silica activity.

ACKNOWLEDGMENTS

We thank Pete J. Dunn of the Smithsonian Institution for making the sample available and for providing preliminary data regarding it. Eliane Desplans carried out the electron-microprobe analyses. We are grateful for the reviews of H.F.W. Taylor, who made many helpful suggestions regarding the phase equilibria, and F. F. Foit, Jr.

REFERENCES CITED

- Hamm, H.-M., and Hentschel, G. (1983) Reinhardbraunsite, $\text{Ca}_3(\text{SiO}_4)_2(\text{OH},\text{F})_2$, a new mineral—The natural equivalent of "calciochondrodite." *Neues Jahrbuch für Mineralogie Monatshefte*, 119–129.
- Imlach, B.V., and Taylor, H.F.W. (1972) Prolonged hydrothermal treatment of cement mixes III. Autoclave curing of C_3S -calcite pastes. *Transactions and Journal of the British Ceramic Society*, 71, 81–83.
- Ingram, L., and Taylor, H.F.W. (1987) ASTM card 29-375. In W.F. McClune, Ed., *Powder diffraction file, Sets 29–30*, Inorganic volume, p. 148. JCPDS International Centre for Diffraction Data, Swarthmore, Pennsylvania.
- Innes, J., and Chaplin, R.C. (1986) Ore bodies of the Kombat mine, South

- West Africa/Namibia. In C.R. Anhaeusser and S. Maske, Eds., *Mineral deposits of southern Africa*, vol. 2, p. 1789–1805. Geological Society of South Africa, Johannesburg.
- Kazak, V.F., Blinov, V.V., and Belov, N.V. (1974) The crystal structure of hydrated tricalcium silicate (TSH). *Doklady Akademia Nauk SSSR*, 219, no. 2, 340–343.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441–450.
- Peacor, D.R., Sarp, H., Dunn, P.J., Innes, J., and Nelen, J.A. (1988) Defernite from the Kombat mine, Namibia: A second occurrence, structure refinement, and crystal chemistry. *American Mineralogist*, 73, 888–893.
- Roy, D.M., and Harker, R.I. (1962) Phase equilibria in the system CaO-SiO₂-H₂O. *Fourth International Symposium on the Chemistry of Cement*, Washington, D.C., 1960, vol. I, p. 196–201. Sponsored by the National Bureau of Standards and Portland Cement Association, Washington, D.C.
- Roy, D.M., and Johnson, A.M. (1967) Investigations of stabilities of calcium silicate hydrates at elevated temperatures and pressures. In *Autoclaved calcium silicate building products, 1965 symposium proceedings*, p. 114–120. Society of Chemical Industry, London.
- Sarp, H., Tanner, M.F., Deferne, J., Bizouard, H., and Liebich, B.W. (1980) La defernite, Ca₂(CO₃)₂(OH,Cl)₈·nH₂O, un nouveau carbonate de calcium chlorohydroxyle. *Bulletin de Minéralogie*, 103, 185–189.
- Taylor, H.F.W. (1962) Hydrothermal reactions in the system CaO-SiO₂-H₂O and the steam curing of cement and cement-silica products. *Fourth International Symposium on the Chemistry of Cement*, Washington, D.C., 1960, vol. I, p. 167–190. Sponsored by the National Bureau of Standards and Portland Cement Association, Washington, D.C.
- (1969) Crystalline calcium silicate hydrates: Equilibria and conditions of formation. *Proceedings of the 5th International Symposium of the Chemistry of Cement*, Tokyo, 1968, vol. 2, p. 1–26. Cement Association of Japan.

MANUSCRIPT RECEIVED DECEMBER 19, 1988

MANUSCRIPT ACCEPTED JUNE 3, 1989