Application of MAS NMR spectroscopy to poorly crystalline minerals: viséite

YEONGKYOO KIM AND R. JAMES KIRKPATRICK

Department of Geology, University of Illinois, Urbana, IL 61801, USA

Abstract

Viséite is a poorly crystalline mineral which is difficult to study by X-ray diffraction pattern. NMR is a very useful technique to study such poorly crystalline minerals, and ^{31}P, ^{27}Al, and ^{29}Si MAS NMR in conjunction with powder XRD results show that at least our viséite sample is not a single phase with a structure analogous to that of analcime as previously reported. Rather, it is very disordered with a structure similar to that of crandallite and includes other phases including an undefined aluminophosphate, opal, and a framework aluminosilicate, probably a zeolite. The previously reported variations in the Si content of viséite are probably due to variable amounts of opal and the framework aluminosilicate.

KEYWORDS: viséite, nuclear magnetic resonance, X-ray diffraction, crystal structure.

Introduction

VISÉITE is an example of a mineral whose structure is not well known due to its diffuse X-ray powder pattern. Spectroscopic methods can be useful in understanding such minerals, and this paper presents ^{27}Al, ^{29}Si, and ^{31}P NMR study of viséite. Viséite is a hydrous basic calcium aluminum silico-phosphate first described by Mélon (1942) as a new mineral from Visé, Belgium. McConnell (1952) studied this mineral by chemical analysis and powder X-ray diffraction (XRD) and concluded that it has a highly defective structure having analogies to the structure of analcime, which has an open framework of corner-linked AlO_4 and SiO_4 tetrahedra (Mazzi and Galli, 1978). The structural formula suggested by McConnell (1952) for the average unit cell of viséite is:

$$(Na_2Ca_{10})[(AlO_2)_{20}(SiO_2)_6(PO_2)_{10}(H_3O_2)_{12}]\cdot16H_2O,$$
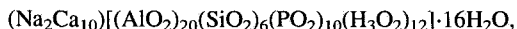
where the PO_4 and $(OH)_4$ tetrahedra are in the same framework as the AlO_4 and SiO_4 tetrahedra.

Later papers questioned the structure of viséite proposed by McConnell (Dunn and Appleman, 1977; Rouse et al., 1989) and concluded that little can be said with certainty about its structural affinities. It is fine-grained, yields diffuse X-ray powder patterns, and shows significant variation in silicon content.

Dunn and Appleman (1977) also reported a significantly different chemical compositions for a viséite sample from Visé and concluded that the variation in silica content is due to admixed opal.

Like viséite, kehoeite has been alleged to be an aluminophosphate isotype of analcime (McConnell and Foreman, 1974), but has been classified as a doubtful species by Fleischer (1987). Recently McConnell (1990) has argued that the structural analogies of the kehoeite and viséite to analcime are valid and that the variations of chemical composition and the diffuse powder patterns are due to their highly defective structures. White and Erd (1992) reexamined kehoeite and concluded that it is not a valid species but is a mixture of quartz, sphalerite, gypsum and woodhouseite. There has been, however, no clear conclusion about the structure of viséite, and this issue is likely to be difficult to address with conventional methods such as XRD because it is fine-grained and so poorly crystalline.

As part of a study of the high-temperature behaviour of analcime, we have examined the NMR characteristics of viséite and concluded that its structure is similar to that of crandallite and that it does not have an analcime-like structure. NMR is an effective probe of local structures of poorly crystalline and amorphous materials (Kirkpatrick, 1988) and it has proven to be an effective method for viséite.

TABLE 1. Chemical analyses of our viséite (A) and viséite from Dunn and Appleman (1977) (B)

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	H_2O
A	3.03	32.89	0.16	0.04	15.46	0.03	0.06	25.90	20.84
B	5.30	33.62	0.15	0.15	17.16	tr.	tr.	28.25	15.37

Experimental

The viséite we examined is from Visé, Belgium (Smithsonian Institution sample R18164). It is pale blue and fine-grained. Powder XRD data were obtained using a Siemens model D500/501 diffract-ometer with a copper target. Due to the diffuse powder pattern of viséite, we used a $0.02°(2\theta)$/step and 12 seconds/step to obtain better resolution.

^{27}Al, ^{31}P, and ^{29}Si MAS NMR spectra were obtained using home-built spectrometers based on 11.7 T and 8.45 T superconducting solenoids (Oxford Instrument) and automated with Nicolet 1280 computers and pulse programmers. ^{27}Al and ^{31}P NMR spectra were collected at $H_o = 11.7$ T (130.3 and 202.4 MHz Larmor frequencies) and MAS frequencies of 9 kHz in a silicon nitride rotor using a 5 mm sample probe manufactured by Doty Scientific. Short (0.5 μs) radio-frequency pulses (solution $\pi/2 = 10$ μs) and 2 s delays between acquisitions were used for ^{27}Al spectra. 3 μs ($\pi/4$) excitation pulses and 10 s delays were used for ^{31}P. The ^{27}Al chemical shifts are reported relative to external 1 M $AlCl_3$ and ^{31}P chemical shifts to 85% H_3PO_4. ^{29}Si spectra were collected at 8.45 T (71.5 MHz) with 7 μs ($\pi/4$) excitation pulses and 20 and 120 s recycle delays. For ^{29}Si, the sample was spun at 3 kHz in a zirconia rotor using a 7 mm probe (Doty Scientific). The ^{29}Si chemical shifts were reported relative to external TMS. For comparison, ^{27}Al and ^{31}P NMR spectra were collected for a crandallite (Smithonian Institution sample 104085-4, Fairfield, Utah) under the same conditions.

The chemical analysis of the viséite was obtained at the Illinois State Geological Survey using X-ray fluorescence (XRF).

Results and discussion

The chemical composition of our viséite is generally similar to that of blue viséite reported by Dunn and Appleman (1977) (Table 1).

The powder XRD pattern of our sample contains several broad and diffuse diffraction lines indicating that it has a highly defective structure (Fig. 1 and Table 2). These lines are in good agreement with those reported by McConnell (1952), except for some

additional small peaks at 6.07 and 5.18 Å. The large peaks at 2.982 and 2.942 Å may have been assigned to one peak by McConnell (1952) due to their breadth. As discussed by McConnell (1952) the XRD peaks of analcime with relative intensities > 5% are similar to those of viséite. The lines with smaller relative intensity, however, do not match well.

The main XRD lines of our viséite and that of McConnell (1956) are also well matched by those of crandallite $(CaAl_3(PO_4)_2(OH)_5 \cdot H_2O)$ reported by others (Table 2). Indeed, except for a few lines with small intensities and the two additional peaks at 5.18 and 6.07 Å, they are in remarkably good agreement.

The ^{31}P MAS NMR spectrum of our sample contains three peaks with chemical shifts of -2.4, -5.2 (the largest), and -13.4 ppm (Fig. 2A). These values are much different from the ^{31}P NMR chemical shift of aluminophosphates and silicoalu-minophosphates with zeolite structures, which are all near -30 ppm (Blackwell and Patton, 1984 and 1988). They are also different from those of $AlPO_4$ phases, which are all in the range of -25 ppm to -30 ppm (Müller et al., 1984). The viséite structure is, thus, very unlikely to be similar to that of a silicoaluminophosphate. However, many Al-phos-phates containing 6-coordinated Al (Al[6]) do have chemical shifts in the range from -4 ppm to -30 ppm (Bleam et al., 1989).

Crandallite is an Al-phosphate with Al[6] and has a chemical shift of -5.2 ppm (Bleam et al., 1989), the same as the largest peak for our sample. Crandallite has only one P-site (Blount, 1974).
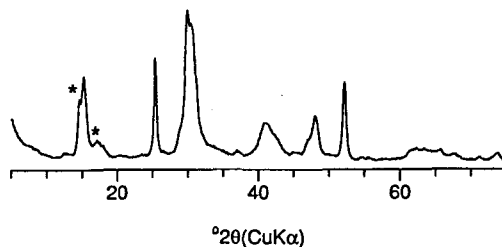

FIG. 1. Powder XRD patterns from our viséite. * indicates impurities.

TABLE 2. Comparison of powder diffraction data for viséite and crandallite ([1]viséite used in this experiment; [2]viséite from McConnell (1952); [3]XRD lines with relative intensity larger than 5% are listed; [4]crandallite from Mrose (1983) (Specimen from Fairfield, Utah, USA); [5]crandallite from Mitchell and Knowlton (1971) (Specimen from Frederick County, Virginia, USA)

Viséite[1]		Viséite[2]		Analcime[3]		Crandallite[4]		Crandallite[5]	
d	I	d	I	d	I	d	I	d	I
6.072	14	—	—	—	—	—	—	—	—
5.833	36	5.68	40	5.60	60	5.698	14	5.70	80
5.177	3	—	—	—	—	—	—	—	—
4.944	2	4.98	10	4.85	20	4.863	20	4.85	70
4.367	1	—	—	—	—	—	—	—	—
—	—	—	—	3.67	8	—	—	—	—
3.508	23	3.46	50	3.43	100	3.503	25	3.51	75
2.982	97	—	—	—	—	2.983	40	2.98	70
2.942	100	2.92	100	2.927	50	2.938	100	2.93	100
2.855	13	—	—	—	—	2.858	5	2.85	10
—	—	—	—	2.693	16	2.699	19	2.70	20
—	—	—	—	2.506	14	—	—	—	—
2.431	1.5	—	—	2.427	8	2.428	4	2.43	40
—	—	—	—	2.226	40	—	—	2.26	10
2.202	19	2.20	20	2.226	40	2.216	8	2.21	60
						2.209	18		
2.186	23.5	—	—	—	—	2.163	60	2.17	70
—	—	2.11	<10	2.118	8	2.137	2	—	—
2.018	1	2.014	<10	—	—	1.9961	2	1.99	10
1.931	7	—	—	—	—	—	—	—	—
1.894	22	1.886	30	1.9041	14	1.8946	45	1.89	80
—	—	—	—	1.8681	8	—	—	—	—
—	—	—	—	—	—	1.8377	6	1.84	10
—	—	—	—	—	—	1.7995	4	1.80	10
1.752	22	1.74	60	1.7430	20	1.7520	35	1.75	80
—	—	—	—	1.7166	6	—	—	—	—
1.677	1	—	—	1.6902	6	1.6841	2	1.69	10
1.655	1	—	—	—	—	1.6478	4	1.65	10
—	—	—	—	—	—	1.6289	2	1.63	10
—	—	—	—	1.5958	6	1.6005	6	1.60	5
—	—	—	—	—	—	1.5645	1	—	—
—	—	—	—	—	—	1.5541	2	1.55	10
		—	—	—	—	1.5178	7		
1.507	1(?)	—	—	—	—	1.5092	3	1.51	20
1.489	6	—	—	—	—	1.4917	6	1.49	40
1.465	1	—	—	—	—	1.4690	10	1.47	40
		—	—			1.4285	25	1.43	50
1.420	1	—	—	1.4163	6	1.4203	5		
1.385	1	1.380	—	—	10			1.39	10
		—	—	—	—	1.3722	4	1.37	10
—	—	—	—	1.3586	8	1.3608	3	1.36	10
—	—	—	—	—	—	1.3442	7	1.34	20
1.324	1	1.323	10	—	—	1.3240	5	1.32	20
1.284	4	1.282	10	—	—	1.2859	7	1.29	50

The ^{31}P NMR spectrum of an impure crandallite obtained from the Smithonian Institution also shows three peaks (Fig. 2B). The main peak (−5.3 ppm) is at the same chemical shift as the crandallite of Bleam *et al.* (1989). The main ^{31}P peak from viséite at −5.2 ppm is, thus, surely from crandallite or a similar phase.
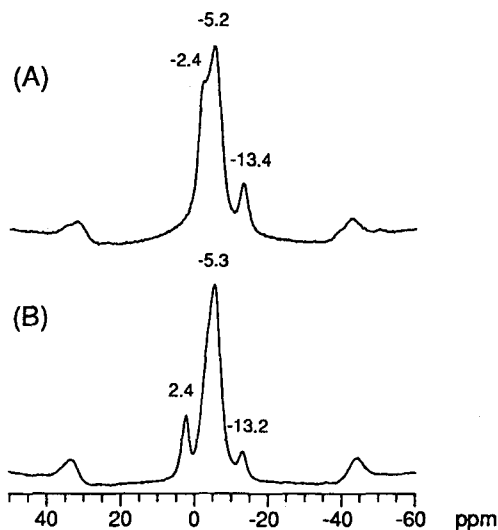
FIG. 2. ^{31}P MAS NMR spectra of viséite (A) and crandallite (B).

FIG. 3. ^{27}Al MAS NMR spectra of viséite (A) and crandallite (B).

The peaks at −13.4 ppm from our viséite sample and −13.2 ppm from our crandallite appear to be from the same or a similar impurity that we cannot currently identify, but which may be commonly associated with aluminum phosphates in nature. The peak at −2.4 ppm from our viséite sample is probably due to an additional Al-phosphate mineral, but the peak at 2.4 ppm for the impure crandallite may be an orthophosphate. Alkali and alkaline earth orthophosphates usually have positive ^{31}P chemical shift (Rothwell et al., 1980; Cheetham et al., 1986; Griffiths et al., 1986; Mudrakovskii et al., 1986; Turner et al., 1986; Hayashi and Hayamizu, 1989). Reported chemical shifts of calcium phosphate are from 0 to 3ppm (Mudrakovskii et al., 1986; Turner et al., 1986) and the chemical shift of calcium hydroxyapatite is 2.8 ppm, close to 2.4 ppm (Rothwell et al., 1980).

The ^{27}Al NMR spectrum of our viséite contains a large peak with a maximum at 4.8 ppm and a small one at 54 ppm (Fig. 3A). ^{27}Al chemical shifts are very sensitive to local environment, especially the nearest neighbor (NN) Al-O coordination (see Kirkpatrick and Phillips, 1993 and references therein). The peak at 4.8 ppm can be easily assigned to Al[6] and the one at 54 ppm to 4-coordinated Al (Al[4]). Framework aluminosilicates yield ^{27}Al chemical shifts with maxima at 11.7 T between 50 ppm and 60 ppm. If viséite had the analcime structure proposed by McConnell (1952 and 1990), we would expect all the ^{27}Al peak intensity to be for Al[4] at 54
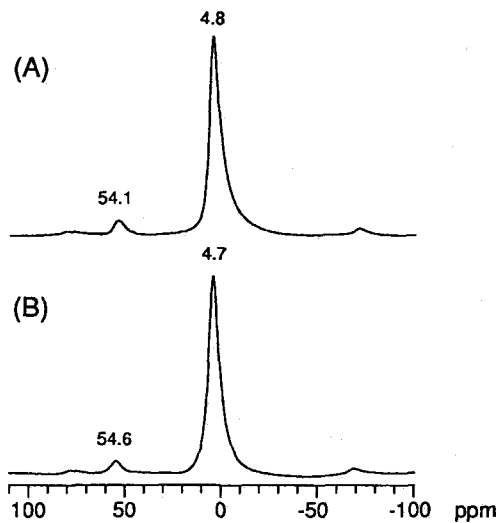
ppm. Thus this spectrum strongly supports the conclusion from ^{31}P NMR that viséite does not have the analcime structure. The structure of crandallite contains Al octahedra in trigonal and hexagonal rings which are linked to form sheets perpendicular to the c axis (Blount, 1974). The ^{27}Al spectrum of our crandallite (Fig. 3B) is essentially identical to that of the viséite, and contains the small peak at 54 ppm. The Al[4]/Al[6] ratios for both the viséite and crandallite are about 0.05. Because the crandallite available to us is impure, it is unclear whether the peak at 54 ppm represents Al[4] in crandallite or an impurity phase. ^{27}Al chemical shifts for Al[4] in aluminophosphates resonate at less positive chemical shifts than those in aluminosilicates (Blackwell and Patton, 1984 and 1988), and the 54 ppm chemical shift is well in the range of aluminosilicates. It is most likely that the peak is due to an aluminosilicate impurity.

The similarity of the XRD patterns, ^{27}Al NMR spectra, and the main ^{31}P NMR peaks between our viséite and crandallite strongly suggest that viséite has a very disordered structure broadly similar to that of crandallite. It also includes additional minerals, probably including an aluminum phosphate, opal, and framework aluminosilicate.

The ^{29}Si MAS NMR spectrum of our viséite collected with a 20 s recycle delay contains one broad peak at −100 ppm and the spectrum collected with a 120 s recycle delay contains additional intensity at −110 ppm. These spectra are noisy due to the low
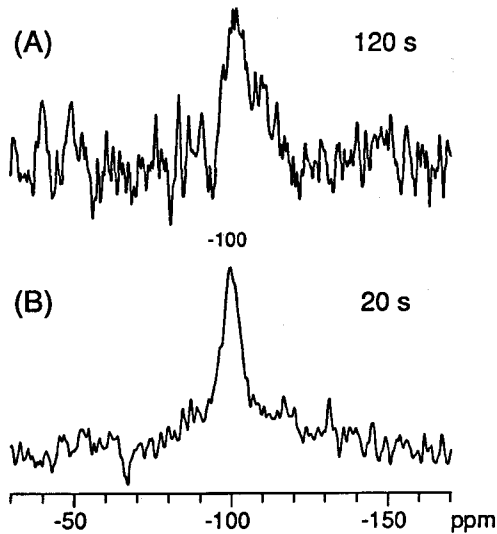
FIG. 4. ^{29}Si MAS NMR spectra of viséite with different delay time between pulses. 20 s (A) and 120 s (B).

Si content, but provide additional insight into the nature of viséite (Fig. 4). Si[4] with $Q^{0,1,2,3}$ polymerization in aluminosilicates typically have chemical shifts less negative than -100 ppm, and Si in Q^4(OAl) sites in the silica polymorphs have more negative chemical shifts (Kirkpatrick, 1988). The chemical shift of -100 ppm indicates that most of the Si in our viséite is in Q^4(1Al) tetrahedra in an impurity framework aluminosilicate such as a feldspar and zeolite (Kirkpatrick, 1988). Although some silicoaluminophosphate molecular sieves have ^{29}Si chemical shifts near -100 ppm (Blackwell and Patton, 1988), the ^{29}Si NMR signal is certainly not due to those phases, considering ^{31}P and ^{27}Al NMR spectra. The shoulder near -110 ppm in the spectrum indicates that there is an additional Si-containing phase with a longer T_1 value. This phase is probably opal, suggested by Dunn and Appleman (1977). Opal has a ^{29}Si chemical shift near -111 ppm and typically has relatively long T_1s (Graetsch et al., 1994).

The small XRD peaks for our sample which do not match those reported for viséite or crandallite are probably due to one or more of the impurity phases.

The range of compositions for viséite reported by Dunn and Appleman (1977) are, thus, due to the presence of varying amounts of impurities. They reported considerable variation in the Si contents and concluded that the Si is from admixed opal. Our NMR data suggest that variations in the amounts of both opal and a framework aluminosilicate are probably the cause of the compositional variation.

References

Blackwell, C.S. and Patton, R.L. (1984) Aluminum-27 and phosphorus-31 nuclear magnetic resonance studies of aluminophosphate molecular sieves. *J. Phys. Chem.*, **88**, 6135−9.

Blackwell, C.S. and Patton, R.L. (1988) Solid-state NMR of silicoaluminophosphate molecular sieves and aluminophosphate materials. *J. Phys. Chem.*, **92**, 3965−70.

Bleam, W.F., Pfeffer, P.E. and Frye, J.S. (1989) ^{31}P solid-state nuclear magnetic resonance spectroscopy of aluminium phosphate minerals. *Phys. Chem. Minerals*, **16**, 455−64.

Blount, A.M. (1974) The crystal structure of crandallite. *Amer. Mineral.*, **59**, 41−7.

Cheetham, A.K., Clayden N.J., Dobson C.M. and Jakeman J.B. (1986) Correlation between ^{31}P N.M.R. chemical shifts and structural parameters in crystalline inorganic phosphates. *J. Chem. Soc. Chem. Commun.*, 195−7.

Dunn, P.J. and Appleman, D.E. (1977) Perhamite, a new calcium aluminum silico-phosphate mineral, and a re-examination of viséite. *Mineral. Mag.*, **41**, 437−2.

Fleischer, M. (1987) *Glossary of Mineral Species* (fifth edition). Mineralogical Record, Tucson, Arizona.

Graetsch, H., Gies, H., and Topalovi (1994) NMR, XRD and IR study on microcrystalline opals. *Phys. Chem. Mineral.*, **21**, 166−75.

Griffiths, L., Root, A., Harris, R.K., Packer, K.J., Chippendale, A.M. and Tromans, F.R. (1986) Magic-angle spinning phosphorus-31 nuclear magnetic resonance of polycrystalline sodium phosphate. *J. Chem. Soc. Dalton Trans.* 2247−51.

Hayashi, S. and Hayamizu, K. (1989) High-resolution solid-state ^{31}P NMR of alkali phosphates. *Bull. Chem. Soc; Jpn.*, **62**, 3061−8.

Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. In: Hawthorne, F.C. (ed.) *Spectroscopic Methods in Mineralogy and Geology.* MAS Reviews in Mineralogy, V.18.

Kirkpatrick, R.J. and Phillips, B.L. (1993) ^{27}Al NMR spectroscopy of minerals and related materials. *Appl. Magn. Reson.*, **4**, 213−36.

Mazzi, F. and Galli, E. (1978) Is each analcime different? *Amer. Mineral.*, **63**, 448−60.

McConnell, D. (1952) Viséite, a zeolite with the analcime structure and containing linked SiO$_4$, PO$_4$, and H$_x$O$_4$ groups. *Amer. Mineral.*, **37**, 609−17.

McConnell, D. (1990) Kehoeite and viséite reviewed: comments on dahllite and francolite. *Mineral. Mag.*, **54**, 657−8.

McConnell, D. and Foreman, D.W. (1974) The structure of kehoeite. *Canad. Mineral.*, **12**, 352–3.

Mélon, J. (1942) La Viséite, nouvelle espece minérale. *Ann. Soc. Géol. Belg.*, **66**, B53–B56.

Mitchell, R.S. and Knowlton, S.M. (1971) Crandallite from Gore, Frederick County, Virginia. *Mineral. Rec.*, **2**, 223–4.

Mrose, M.E. (1983) *Mineral Powder Diffraction File*, JCPDS, 30pp.

Mudrakovskii, V.P., Shmachkova, N.S. and Kotsarenko, N.S. (1986) ^{31}P NMR study of I-IV group polycrystalline phosphates. *J. Phys. Chem. Solids*, **47**, 335–9.

Müller, D., Jahn, E., Ladwig, G. and Haubenreisser, U. (1984) High-resolution solid-state ^{27}Al and ^{31}P NMR: Correlation between chemical shift and mean Al-O-P angle in AlPO$_4$ polymorphs. *Chem. Phys. Lett.*, **109**, 332–6.

Rothwell, W.P., Waugh, J.S. and Yesinowski, J.P. (1980) High-resolution variable temperature ^{31}P NMR of solid calcium phosphates. *J. Amer. Chem. Soc.*, **102**, 2637–43.

Rouse, R.C., Peacor, D.R. and Merlino, S. (1989) Crystal structure of pahasapaite, a beryllophosphate mineral with a distorted zeolite rho framework. *Amer. Mineral.*, **74**, 1195–1202.

Turner, G.L., Smith, K.A., Kirkpatrick, R.J. and Oldfield, E. (1986) Structure and cation effects on phosphorus-31 NMR chemical shift and chemical-shift anisotropies of orthophosphates. *J. Mag. Res.*, **70**, 408–15.

White, J.M. and Erd, R.C. (1992) Kehoeite is not a valid species. *Mineral. Mag.*, **56**, 256–8.