

Appendix Table 1. Frequencies of the lattice vibrations (ν_i), the temperature dependence and the isobaric mode Grüneisen parameters.

Humite			Norbergite		
ν_i (cm ⁻¹)	$(\partial\nu_i/\partial T)_P$ (cm ⁻¹ /K)	γ_{iP}	ν_i (cm ⁻¹)	$(\partial\nu_i/\partial T)_P$ (cm ⁻¹ /K)	γ_{iP}
153	-0.013(3)	2.331(1)	199	-0.012(9)	1.654(9)
193	-0.022(3)	3.098(5)	225	-0.022(5)	2.553(1)
204	-0.018(9)	2.484(5)	257	-0.022(2)	2.185(4)
274	-0.012(7)	1.243(1)	290	-0.016(9)	1.487(8)
325	-0.021(2)	1.749(3)	329	-0.020(4)	1.583(1)
356	-0.027(1)	2.033(9)	380	-0.026(2)	1.760(2)
384	-0.010(2)	0.712(3)	429	-0.021(8)	1.297(3)
432	-0.023(5)	1.458(8)	489	-0.016(5)	0.861(4)
467	-0.029(4)	1.688(3)	517	-0.008(2)	0.404(9)
502	-0.034(1)	1.821(6)	555	-0.010(7)	0.492(2)
538	-0.005(3)	0.264(2)	573	-0.009(7)	0.432(2)
578	-0.022(1)	1.025(3)	611	-0.018(1)	0.756(3)
604	-0.016(8)	0.745(9)	770	-0.042(2)	1.399(2)
755	0.0002(1)	-0.007(1)	792	-0.009(9)	0.319(1)
783	-0.007(8)	0.267(1)	851	-0.014(9)	0.447(1)
843	-0.014(7)	0.467(6)	885	-0.026(2)	0.755(8)
865	-0.005(8)	0.179(8)	894	-0.020(3)	0.579(7)
932	-0.026(1)	0.751(1)	951	-0.023(1)	0.620(1)
968	-0.025(6)	0.709(2)	973	-0.035(2)	0.923(6)

Appendix Table 2. Frequencies of the OH-stretching vibrations, the temperature dependence and the isobaric mode Grüneisen parameters.

Mineral	ν_i (cm ⁻¹)	$(\partial\nu_i/\partial T)_P$ (cm ⁻¹ /K)	γ_{iP}
Norbergite	3582 ^a	-0.023(7)	0.168(9)
	3315 ^b	0.023(1)	-0.177(9)
	3365 ^b	0.023(9)	-0.181(3)
	3581 ^b	-0.025(9)	0.184(6)
	3665 ^b	-0.043(9)	0.305(8)
Humite	3390 ^a	0.010(9)	-0.086(2)
	3556 ^a	-0.014(6)	0.110(1)
	3568 ^a	-0.013(6)	0.102(2)
	3333 ^b	0.026(9)	-0.216(4)
	3381 ^b	0.024(8)	-0.196(7)
	3556 ^b	-0.047(2)	0.355(9)
	3573 ^b	-0.028(2)	0.210(2)
Clinohumite	3310 ^a	0.053(1)	-0.458(6)
	3405 ^a	0.018(8)	-0.158(3)
	3528 ^a	-0.025(2)	0.204(9)
	3565 ^a	-0.022(7)	0.182(6)
	3309 ^b	0.015(8)	-0.136(8)
	3397 ^b	0.021(8)	-0.183(8)
	3529 ^b	-0.027(6)	0.224(1)
	3564 ^b	-0.022(9)	0.184(1)
	3608 ^b	-0.041(7)	0.331(1)

a: Raman-active OH bands; b: IR-active OH bands.

Appendix Table 3. Raman and infrared measurements for humite-group minerals with various fluorine and titanium concentrations under ambient condition. The integral intensities below and above 3450 cm^{-1} are estimated from the reported spectra.

Mineral	X_{Ti}	X_{F}	$I_{<3450}/I_{>3450}$	Reference
F-rich ($X_{\text{F}} \geq 0.33$) samples by FTIR measurements (Fig. 7a)				
Chondrodite	0.05	0.73	0.47(5)	Williams (1992)
Chondrodite	0.02	0.88	0.25(3)	Cynn et al. (1996)
Chondrodite	0.02	0.37	0.42(4)	Kuribayashi et al. (2004)
Humite	0.016	0.33	0.43(2)	This study
Norbergite	0.03	0.63	0.85(3)	--
Ti-rich ($X_{\text{Ti}} \geq 0.08$) samples by FTIR measurements (Fig. 7b)				
Clinohumite	0.45	0	4.81(5)	Shen et al. (2014)
Clinohumite	0.33	0	3.36(3)	--
Clinohumite	0.18	0	2.45(2)	--
Chondrodite	0.36	0	5.21(5)	--
Chondrodite	0.29	0	3.92(4)	--
Clinohumite	0.25	0.13	2.97(1)	Liu et al. (2019a)
Clinohumite	0.45	0.01	7.31(7)	Koga et al. (2014)
Clinohumite	0.43	0.01	7.12(7)	--
Clinohumite	0.46	0.01	9.75(9)	--
Clinohumite	0.41	0.14	4.11(4)	--
Clinohumite	0.39	0.17	3.26(3)	--
Ti-rich ($X_{\text{Ti}} \geq 0.08$) samples by Raman measurements (Fig. 7c)				
Clinohumite	0.08	0	0.92(9)	Frost et al. (2007)
Clinohumite	0.21	0	1.16(9)	Frost et al. (2007)
Clinohumite	0.25	0.2	1.29(1)	Liu et al. (2019a)
Clinohumite	0.46	0.01	4.14(4)	Koga et al. (2014)
Clinohumite	0.43	0.01	3.25(3)	--
Clinohumite	0.39	0.17	1.16(9)	--
Clinohumite	0.41	0.14	6.75(7)	--

X_{F} is F/(F+OH) in moles. X_{Ti} is the fraction of Ti at the M3 site.