Revision 1 1 2 Si-rich Mg-sursassite Mg₄Al₅Si₇O₂₃(OH)₅ with octahedrally-coordinated Si: a 3 new ultra-high-pressure hydrous phase 4 5 LUCA BINDI^{1,2,*}, MARK D. WELCH³, ALEKSANDRA A. BENDELIANI^{4,5}, ANDREY V. BOBROV^{4,5,6} 6 7 8 ¹Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy 9 ²C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy 10 ³Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom ⁴Geological Faculty, Moscow State University, Moscow 119991, Russia 11 ⁵Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow 119991, 12 13 Russia ⁶Korzhinskii Institute of Experimental Mineralogy, Chernogolovka, Moscow oblast 142432, Russia 14 15 *Corresponding Author: luca.bindi@unifi.it 16

17

ABSTRACT

The crystal structure of a new high-pressure hydrous phase, Si-rich Mg-sursassite, of ideal 18 composition Mg₄Al₅Si₇O₂₃(OH)₅, that was produced by sub-solidus reaction at 24 GPa and 1400 19 °C in an experiment using a model sedimentary bulk composition, has been determined by 20 single-crystal X-ray diffraction. The phase was found to be topologically identical to Mg-21 sursassite, Mg₅Al₅Si₆O₂₁(OH)₇, and has space group $P2_1/m$ and lattice parameters a = 8.4222(7), 22 b = 5.5812(3), c = 9.4055(9) Å, $\beta = 106.793(8)^{\circ}, V = 423.26(6)$ Å³ and Z = 1. The empirical 23 formula determined by electron microprobe analysis of the same crystal as was used in the X-ray 24 experiment is $[Mg_{3.93(3)}Fe_{0.03(1)}]_{\Sigma 3.96}[Al_{4.98(3)}Cr_{0.04(1)}]_{\Sigma 5.02}Si_{7.02(4)}O_{23}(OH)_5$, with hydroxyl content 25 implied by the crystal structure analysis. The most significant aspect of the structure of Si-rich 26 Mg-sursassite is the presence of octahedrally-coordinated Si. Its structural formula is ^{M1,VII}Mg₂ 27 ${}^{\textit{M2,VI}}Mg^{2+}{}_2 \; {}^{\textit{M3,VI}}(Al_{0.5}Si_{0.5})_2 \; {}^{\textit{M4,VI}}Al_2 \; {}^{\textit{M5,VI}}Al_2 \; {}^{\textit{T1,IV}}Si_2 \; {}^{\textit{T2,IV}}Si_2 \; {}^{\textit{T3,IV}}Si_2 \; {}^{\textit{O23}}(OH)_5.$ Si-rich Mg-28 sursassite joins the group of hydrous ultra-high-pressure phases with octahedrally-coordinated Si 29 that have been discovered by experiment, and that may play a significant role in the distribution 30 and hosting of water in the deep mantle at subduction zones. The reactions defining the stability 31

of Si-rich Mg-sursassite are unknown, but are likely to be fundamentally different from those of
 Mg-sursassite, and involve other ultra-high-pressure dense structures such as Phase D, rather
 than Phase A.

35

36 Keywords: Mg-sursassite; hydrous dense magnesium silicate; synthesis; microprobe analysis;

37 X-ray diffraction; crystal structure.

- 38
- 39

INTRODUCTION

40 Sursassite, ideally $Mn_4Al_6Si_6O_{22}(OH)_6$, occurs in Mn ore deposits (Nagashima et al. 2009), and is characteristically a low-pressure mineral. It is a sorosilicate with Si_2O_7 and SiO_4 groups 41 that is related structurally to pumpellyite and ardennite. However, a fully Mg-substituted 42 43 analogue of composition $Mg_5Al_5Si_6O_{21}(OH)_7$ was first reported by Schreyer (1988) in 44 experiments in the MgO-Al₂O₃-SiO₂-H₂O (MASH) system up to 5 GPa, 900 °C; he referred to this phase as "MgMgAl-pumpellyite". Fockenburg (1998) determined the maximum stability of 45 this phase to 10 GPa and found that it had a thermal limit of 800 °C defined by the reactions Mg-46 sursassite = pyrope + topaz-OH + coesite/stishovite + H_2O . Using a model ultrabasic bulk 47 composition, Bromiley and Pawley (2002) determined the phase relations of Mg-sursassite to 10 48 49 GPa, and showed that Mg-sursassite replaces chlorite as a major host of H₂O above 6 GPa via the reaction chlorite + enstatite = Mg-sursassite + forsterite + H_2O . The high-temperature limit of 50 Mg-sursassite at 7-10 GPa (700-750 °C) for ultrabasic bulk compositions is defined by the 51 52 reaction Mg-sursassite + phase A + enstatite = $pyrope + H_2O$. The general structural formula of sursassite-group minerals is ${}^{M1,VII}M^{2+}{}_{2}{}^{M2,VI}M^{2+}{}_{2}{}^{M3,VI}(M^{2+},Al,Si){}_{2}{}^{M4,VI}Al{}_{2}{}^{M5,VI}Al{}_{2}{}^{T1,IV}Si{}_{2}{}^{T2,IV}Si{}_{2}$ 53 ^{73,IV}Si₂ O₂₁₋₂₃(OH)₅₋₇. ⁷²Si and ⁷³Si form a sorosilicate Si₂O₇ unit. Occupancies of H sites vary 54 from 0.5 to 1. Compositional variation in sursassite-type phases involves (a) homovalent 55 substitution at M(1,2) sites, e.g. Mg, Mn^{2+} , Fe^{2+} ; (b) heterovalent substitution at the M3 site, e.g. 56 Mg for Al; (c) charge balancing by $O^{2-} \rightarrow OH^{-}$. Two distinct stoichiometries have been reported: 57 $M^{2+}_{4}Al_{6}Si_{6}O_{22}(OH)_{6}$ and $M^{2+}_{5}Al_{5}Si_{6}O_{21}(OH)_{7}$, being related by the substitution $Al + O^{2-} \leftrightarrow M^{2+}$ 58

+ OH⁻. In this paper we add a new stoichiometry, $M^{2+}_{4}Al_{5}Si_{7}O_{23}(OH)_{5}$, which we refer to as Sirich Mg-sursassite.

61 In sursassite sensu stricto the M3 site is fully occupied by A1 and there are five nonequivalent H sites bonded to three non-equivalent oxygen atoms; four of the H sites are half-62 occupied (Nagashima et al. 2009). The M3 site in Mg-sursassite has an average composition 63 Mg_{0.5}Al_{0.5} and there are four non-equivalent H sites, one of which is half-occupied. The 64 structural formula of end-member Mg-sursassite is ^{M1,VII}Mg2^{M2,VI}Mg²⁺2^{M3,VI}(Mg05Al05)2^{M4,VI}Al2 65 ^{M5,VI}Al₂^{T1,IV}Si₂^{T2,IV}Si₂^{T3,IV}Si₂O₂₂(OH)₇. As described below, the new phase Si-rich Mg-sursassite 66 has the structural formula ${}^{M1,VII}Mg_2 {}^{M2,VI}Mg^{2+}_2 {}^{M3,VI}(Al_{0.5}Si_{0.5})_2 {}^{M4,VI}Al_2 {}^{M5,VI}Al_2 {}^{T1,IV}Si_2 {}^{T2,IV}Si_2$ 67 ^{*T*3,IV}Si₂O₂₃(OH)₅. The possible significance of this new type of sursassite is considered. 68

- 69
- 70

EXPERIMENTAL METHODS

71 A high-pressure experiment was performed at 24 GPa and 1400°C using a 2000-ton Kawai-type multi-anvil apparatus at the Geodynamics Research Center, Ehime University, 72 Matsuyama, Japan. A sintered mixture of 83%MgO + 17% CoO was used as the pressure 73 medium. This mixture was formed into an octahedron of 8 mm edges and was compressed by 74 eight cubic tungsten carbide anvils with 3 mm truncation edges. Pyrophyllite gaskets were placed 75 76 between the anvils to support the anvil flanks. A cylindrical LaCrO₃ heater, 3.2/2.0 mm in outer/inner diameter and 4 mm long was used. The samples were loaded into rhenium capsules 77 78 isolated from heater by a MgO insulator.

The starting material, chosen to model "global subducted sediment" (GLOSS) of Plank and Langmuir (1998), was a mixture of high-purity reagents (in wt%): 58.66 SiO₂, 0.62 TiO₂, 11.93 Al₂O₃, 5.96 CaO, 5.22 FeO, 2.49 MgO, 0.32 MnO, 2.44 Na₂O, 2.04 K₂O, 3.02 CO₂ and 7.30 H₂O. Temperature was controlled by a W₉₇Re₃-W₇₅Re₂₅ thermocouple (0.1 mm diameter). Pressure was calibrated at room temperature using the semiconductor-to-metal transitions of Bi, ZnS and GaAs (Irifune et al. 2004). The sample was initially pressurized to 24 GPa in 1 hour and then heated to 1400 °C at a rate of 50°C/min. The effect of temperature on pressure was further

corrected using the α - β and β - γ transitions in Mg₂SiO₄ (Katsura and Ito 1989). The experiment lasted 4 hours and was quenched by turning off power to the heater. The capsule was recovered, mounted in epoxy, sectioned, and polished.

- 89
- 90

CHEMICAL AND STRUCTURAL CHARACTERIZATION

The chemical composition of Mg-sursassite was first analyzed qualitatively with energy-91 dispersive X-ray spectroscopy (EDS) using a CamScan electron microscope MV2300. No 92 elements with Z > 9 other than Al, Mg, Si and minor Cr and Fe were detected. A small fragment 93 of the of crystal analyzed by EDS ($15 \times 18 \times 24 \ \mu m^3$) was extracted from the polished block for 94 crystal structure determination by single-crystal X-ray diffraction (see below). After the X-ray 95 experiment, this crystal fragment was analyzed by quantitative wavelength-dispersive X-ray 96 (WDS) using a JEOL-JXA 8200 microprobe operated at 15 kV, 10 nA, and 1 µm beam size, with 97 98 counting times of 20 s on-peak and 10 s for each background position. K α lines for all analyzed elements were referenced to synthetic mineral standards [olivine (Mg, Fe, Si), albite (Al), and 99 knorringite (Cr)]. 100

101 The crystal fragment was mounted on a 5 μ m diameter carbon fiber, itself attached to a 102 glass rod. Single-crystal X-ray diffraction intensity data were collected with a Bruker D8 103 Venture Photon 100 CMOS equipped with graphite-monochromatized Mo*K* α radiation. The 104 detector-to-crystal distance was 50 mm. Data were collected using ω and φ scan modes, with a 105 0.5° frame-width and an exposure time of 50 s per frame. The data were corrected for Lorentz 106 and polarization factors and absorption using the software package *APEX3* (Bruker AXS Inc. 107 2016).

108

109

RESULTS AND DISCUSSION

Phases in the run product were identified using EMPA and single-crystal XRD. The
product assemblage consisted of (vol%) Si-rich Mg-sursassite (1%) + phase D (20%) +

hollandite (13%) + Al-phase D (13%) + Ca-perovskite (15%) + stishovite (38%) (Fig. 1). The
compositions of run products are shown in Table 1.

As for the studied Si-rich sursassite, three very similar analyses were obtained by WDS 114 microprobe analysis. The average has in wt% oxides (ranges in parentheses): MgO = 17.87 115 (17.69-17.93), Al₂O₃ = 28.66 (28.32-29.01), FeO = 0.29 (0.19-0.40), Cr₂O₃ = 0.37 (0.29-0.49), 116 $SiO_2 = 47.64$ (47.40–48.11), total = 94.83 (94.22–95.05). The H₂O content, calculated from the 117 crystal structure analysis (see below), is 5.09 wt%, which gives an analysis total of 99.92 wt%. 118 The empirical formula (16 cations p.f.u.), assuming all Fe is divalent, all Cr is trivalent, and a 119 120 H_2O content calculated from the ideal formula $Mg_4Al_5Si_7O_{23}(OH)_5$, is $[Mg_{3,93(3)}Fe_{0,03(1)}]_{\Sigma_{3,96}}[Al_{4,98(3)}Cr_{0,04(1)}]_{\Sigma_{5,02}}Si_{7,02(4)}O_{23}(OH)_{5}$. The minor Cr content (not present in 121 the starting material) is likely due to a contamination from the LaCrO₃ heater. 122

123 The diffraction data indicate that the structure is monoclinic. Systematic absences are 124 consistent with space groups $P2_1$ and $P2_1/m$. Unit-cell parameters obtained from least-squares refinement of 198 reflections with $I/\sigma(I) > 10$ are a = 8.4222(7), b = 5.5812(3), c = 9.4055(9) Å, 125 $\beta = 106.793(8)^{\circ}$, V = 423.26(6) Å³. The unit-cell parameters and $P2_1/m$ symmetry indicated a 126 close correspondence with those of synthetic Mg-sursassite reported by Gottschalk et al. (2000), 127 for which a = 8.5424(8), b = 5.5717(3), c = 9.6484(6) Å, $\beta = 108.298(4)^{\circ}$, V = 447.0(1) Å³. 128 129 Consequently, the atom coordinates of the structure of Mg-sursassite reported by Gottschalk et al. (2000) were used as the starting model for structure refinement by full-matrix least-squares 130 131 methods using SHELXL-97 (Sheldrick 2008).

Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). In refining site-scattering at sites, vacancies were allowed on all *M* sites. Initially, site-scattering values were obtained by allowing unconstrained occupancies of sites using Mg (M1, M2), Al (M4, M5) and Si (M3, T1, T2, T3). Refined occupancy levels indicated that M1 and M2 are filled by Mg, whereas M4 and M5 are filled by Al. However, the refined occupancy of M3 using a neutral scattering factor for Si is 0.967(2) and corresponds to 13.47(2) electrons. Hence, the most reasonable interpretation of the site-scattering at M3 is that this site has an occupancy of $Al_{0.5}Si_{0.5}$. The high Si occupancy of this site is consistent with the small volume of the *M*3 octahedron (7.53 Å³), which is much smaller than 9.40 Å³ for ^{*M*3}AlO₆ in sursassite (Nagashima et al. 2009) and 10.30 Å³ for ^{*M*3}(Mg_{0.5}Al_{0.5})O₆ in Mg-sursassite (Gottschalk et al. 2000). The SiO₆ octahedron in stishovite has a volume of 6.61 Å³ (Hill et al. 1983). Thus, there is compelling evidence from chemistry and structure that the crystal of this study has stoichiometric amounts of excess Si relative to Mg-sursassite and that this excess Si is octahedrally-coordinated Si.

On the basis of refined site-scattering values, the occupancies of sites were fixed at M(1,2)= Mg, $M3 = (Al_{0.5}Si_{0.5}), M(4,5) = Al, T(1,2,3) = Si$ for subsequent anisotropic refinement. With full anisotropic refinement to convergence gave agreement indices of $R_1 = 0.040, wR_2 = 0.074$, GoF = 0.935. Unsurprisingly for such a small crystal, no hydrogen atoms were located in difference-Fourier maps.

A list of observed and calculated structure factors and the CIF are deposited¹. Details relating to the data collection and structure refinement are given in Table 2. Table 3 gives bondvalence sums (BVS), computed on the basis of bond-valence parameters of Brese and O'Keeffe (1991), for cations and oxygen atoms. The key features of the structure of Si-rich Mg-sursassite is summarized in Figure 2.

The interpretation of oxygen donors and acceptors in sursassite-group structures requires some care, as there are half-occupied and fully-occupied H sites, and mixed occupancies of cation sites. In the case of sursassite *sensu stricto*, these issues have been addressed in detail by Nagashima et al. (2009), and we have used their analysis to aid interpretation of the bondvalences of some of the more problematic oxygen atoms in Si-rich Mg-sursassite, namely O(5), O(7) and O(10).

¹ For a copy of the list of observed and calculated structure factors and CIF, document item AMxxxxx, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <u>http://www.minsocam.org</u>.

162 In Si-rich Mg-sursassite, atoms O(6) (BVS = 1.21 v.u.) and O(11) (BVS = 1.16 v.u.) are obvious oxygen donors for OH groups and are very likely to be associated with fully-occupied H 163 atom sites. The BVS values for O(7) and O(10) are very similar to those of sursassite. As pointed 164 out by Nagashima et al. (2009), O(10) is anomalous in that it is two-coordinate, being bonded 165 only to ^{T1}Si and ^{M2}Mn (^{M2}Mg in Mg-sursassite and Si-rich Mg-sursassite). There is no evidence 166 for protonation of this oxygen atom, as occurs in the related mineral macfallite (Nagashima et al. 167 2008), e.g. location of nearby H or lengthening of the Si1-O(10) bond. There is, however, the 168 169 likelihood of O(10) receiving a strong hydrogen-bond from O(6)H, thereby raising its BVS value to ~ 1.7 v.u. (Nagashima et al. 2009): d[O(6)...O(10)] = 2.80 Å. 170

The O(7) atom is bonded to two M3 and one Mg1 sites. There are two possibilities for 171 assigning its bond-valence deficiency: (a) O(7) receives a strong hydrogen-bond from O(6), or 172 173 (b) O(7) = 50% O/50% OH. How might we choose between these two options? The composition 174 of Si-rich Mg-sursassite is very well-defined by EMPA (see above). The cation composition 4Mg:5Al:7Si requires 51 negative charges to charge-balance. There are 28 oxygens p.f.u and so 175 five of these must be OH. O(6) and O(11) are fully-occupied OH groups. Hence, an additional 176 half-occupied OH group must be present that would have an oxygen atom BVS of ~1.5 v.u: 177 atoms O(7) and O(10) are the only candidates. However, we have seen above that O(10) is very 178 179 unlikely to be an OH group, half- or fully-occupied. This leaves O(7) as the only other possibility. This atom also correlates with a hydroxyl group in sursassite (M3 = AI) and Mg-180 sursassite ($M3 = Mg_{0.5}Al_{0.5}$). Hence, it would seem reasonable to propose that it is a 50/50 O/OH 181 site in Si-rich Mg-sursassite; O(6) with which it likely forms a strong hydrogen bond has two 182 half-occupied H sites and so has full OH occupancy overall (as its BVS value of 1.21 v.u. 183 184 indicates). The corresponding configuration occurs in sursassite (Nagashima et al. 2009).

185

186

IMPLICATIONS

The experiment reported in this paper was a synthesis, and as such it is not proof *sensu stricto* of the thermodynamic stability under these *P-T* conditions of any of the product phases.

However, as noted above, Si-rich Mg-sursassite grew at 24 GPa during heating to 1400 °C and
persisted to the end of the experiment. This temperature is much higher than the 800 °C limit at
10 GPa of Mg-sursassite (Fockenburg 1998).

The presence of octahedrally-coordinated Si in Si-rich Mg-sursassite suggests that the reactions defining its *P-T* stability in ultrabasic and basic bulk compositions are likely to be fundamentally different from those of Mg-sursassite (which, in turn, has a much greater *P-T* stability than sursassite), and involve ultra-high-pressure structures such as Phase D, rather than Phase A. Future experiments at 10–25 GPa and 800-1400 °C on ultrabasic, basic and felsic model bulk compositions, and on Si-rich Mg-sursassite itself, should provide insights into the significance of this phase for the hydrous mineralogy of deep subduction.

- 199
- 200

ACKNOWLEDGMENTS

The paper benefited by the official reviews from Wilson Crichton and an anonymous reviewer. These experiments were a part of the scientific program of the Laboratory of Deep Geospheres, Geological Faculty, Moscow State University, and were supported by the Russian Science Foundation, project no. 17-17-01169. A.A.B. thanks the Geodynamics Research Center, Ehime University, Matsuyama, Japan, for support of her visit in 2019.

- 206
- 207

REFERENCES CITED

- Brese, N.E., and O'Keeffe, M. (1992) Bond-valence parameters for solids. Acta
 Crystallographica, B47, 192–197.
- Bromiley, G.D., and Pawley, A.R. (2002) The high-pressure stability of Mg-sursassite in a model
 hydrous peridotite: A possible mechanism for the deep subduction of significant volumes
 of H₂O. Contributions to Mineralogy and Petrology, 142, 714–723.
- Bromiley, G.D., and Pawley, A.R. (2003) The stability of antigorite in the systems MgO-SiO₂-H₂O (MSH) and MgO-Al₂O₃-SiO₂-H₂O (MASH): the effects of Al³⁺ substitution on
- high-pressure stability. American Mineralogist, 88, 99–108.

- 216 Bruker (2016) APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- 217 Fockenberg, T. (1998) An experimental study of the pressure-temperature stability of MgMgAl-
- pumpellyite in the system $MgO-Al_2O_3-SiO_2-H_2O$. American Mineralogist, 83, 220–227.
- Gottschalk, M., Fockenberg, T., Grevel, K.-D., Wunder, B., Wirth, R., Schreyer, W., and 219 W.V. (2000)220 Maresch, Crystal structure of the high-pressure phase $Mg_4(MgAl)Al_4[Si_6O_2/(OH)_7]$: an analogue of sursassite. European Journal of 221 Mineralogy, 12, 935-945. 222
- Hill, R.J., Newton, M.D., and Gibbs, G.V. (1983) A crystal chemical study of stishovite. Journal
 of Solid State Chemistry, 47, 185–200.
- Irifune, T., Kurio, A., Sakamoto, S., Inoue, T., Sumiya. H., and Funakoshi, K. (2004) Formation
 of pure polycrystalline diamond by direct conversion of graphite at high pressure and high
 temperature. Physics of the Earth and Planetary Interiors, 143–144, 593–600.
- Katsura, T., and Ito, E. (1989) The system Mg₂SiO₄-Fe₂SiO₄ at high pressure and temperatures:
 Precise determination of stabilities of olivine, modified spinel, and spinel. Journal of
 Geophysical Research, 94, 15663–15670.
- Nagashima, M., Akasaka, M., Minakawa, T., Libowitzky, E., and Armbruster, T. (2009)
 Sursassite: hydrogen bonding, cation order, and pumpellyite intergrowth. American
 Mineralogist, 94, 1440–1449.
- Nagashima, M., Rahmoun, N.S., Alekseev, E.V., Geiger, C.A., Armbruster, T., and Akasaka, M.
 (2008) Crystal chemistry of macfallite: Relationships to sursassite and pumpellyite.
 American Mineralogist, 93, 1851–1857.
- Plank, T., and Langmuir, C.H. (1998) The chemical composition of subducting sediment and its
 consequences for the crust and mantle. Chemical Geology, 145, 325–394.
- Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112–122.
- Schreyer, W. (1988) Experimental studies on metamorphism of crustal rocks under mantle
 pressures. Mineralogical Magazine, 52, 1–26.

Wilson, A.J.C., Ed. (1992) International Tables for Crystallography, Volume C: Mathematical,
physical and chemical tables. Kluwer Academic, Dordrecht, NL.

244

245

FIGURE CAPTIONS

Figure 1. SEM-BSE image of the experimental run synthesized at P = 24 GPa and T = 1400 °C. Si-rich Mg-sursassite (Si-Sur) is associated with phase δ , hollandite (holl), stishovite (Sti), phase D, and Ca-perovskite (CaPrv). CamScan electron microscope MV2300.

Figure 2. (a) View of the structure of Si-rich Mg-sursassite determined in this study projected 249 onto the (010) plane. Blue = isolated SiO₄ and Si₂O₇ sorosilicate groups, pink = M4250 and M5 octahedra (Al), green = M3 octahedron (50%Al, 50%Si), orange spheres = M1251 (Mg) and M2 (Mg). Rows of M(2,3,4,5) octahedra and ^{VII}M1 polyhedra extend into the 252 253 page parallel to [010]. (b) A fragment of a row of M3 octahedra in Si-rich Mg-254 sursassite showing the coordination of O(5) and O(7) oxygen atoms. The two O(1)atoms of the M3O₆ octahedron have been omitted for clarity. The proposed local 255 ordering of Al and Si in the M3 sites is indicated. All atoms are shown as displacement 256 ellipsoids at the 68% probability level. 257

259

258

260

and phase D) or oxygen content (Holl and Ca-Prv)									
Phase	δ	D	Holl	Ca-Prv					
SiO ₂	13.99	38.39	38.39 65.97						
TiO ₂	0.86	0.21	-	0.16					
Al_2O_3	63.48	23.40	19.70	-					
FeO	2.47	6.61	0.31	0.57					
MnO	-	0.15	-	-					
MgO	5.85	17.25	0.36	0.54					
CaO	-	0.05	0.60	40.26					
Na ₂ O	-	-	0.53	0.23					
K ₂ O	0.09	-	12.80	-					
H_2O^*	14.77	13.88	-	-					
Total	101.51	99.94	100.27	99.34					
0	-	-	8	3					
Si	0.139	1.181	2.984	1.079					
Ti	0.006	0.005	-	0.002					
Al	0.746	0.848	1.050	-					
Fe	0.021	0.170	0.012	0.009					
Mn	-	0.004	-	-					
Mg	0.087	0.790	0.024	0.015					
Ca	-	0.002	0.029	0.808					
Na	-	-	0.046	0.008					
K	0.001	-	0.738	-					
Total	1.000	3.000	4.883	1.921					

Table 1. Microprobe data (wt. % of oxides) of the different phases in the run product together with the atomic ratios calculated on the basis of atoms (phase δ and phase *D*) or oxygen content (*Holl* and *Ca-Prv*)

Crystal data	
Formula Crystal size (mm) Form Colour Crystal system Space group a (Å) b (Å) c (Å) β (°) V (Å ³) Z	$\begin{array}{l} Mg_{4}Al_{5}Si_{7}O_{23}(OH)_{5} \\ 0.015 \times 0.018 \times 0.024 \\ block \\ white \\ monoclinic \\ P2_{1}/m \ (\#11) \\ 8.4222(7) \\ 5.5812(3) \\ 9.4055(9) \\ 106.793(8) \\ 423.26(6) \\ 1 \end{array}$
Data collection	
Instrument Radiation type Temperature (K) Detector to sample distance (cm) Number of frames Measuring time (s) Maximum covered 2θ (°) Absorption correction Collected reflections Unique reflections Reflections with $F_0 > 4\sigma(F_0)$ R_{int} R_{σ} Range of <i>h</i> , <i>k</i> , <i>l</i>	Bruker D8 Venture MoK α ($\lambda = 0.71073$) 295(3) 5 1102 50 66.08 multi-scan 3488 1734 850 0.0228 0.0834 -12 $\leq h \leq 11, -8 \leq k \leq 8, 0 \leq l \leq 13$
Refinement	
Refinement Final $R_1 [F_0 > 4\sigma(F_0)]$ Final R_1 (all data) Number refined parameters GoF $\Delta \rho_{max}$ (e Å ⁻³) $\Delta \rho_{min}$ (e Å ⁻³)	Full-matrix least squares on <i>F</i> ² 0.0343 0.0401 124 0.935 0.50 -0.39

Table 2. Data and experimental details for the selected Si-rich Mg-sursassite crystal

_

	<i>M</i> 1	M2	<i>M</i> 3	<i>M</i> 4	<i>M</i> 5	<i>T</i> 1	<i>T</i> 2	<i>T</i> 3	ΣΟ
	(Mg)	(Mg)	$(Al_{0.50}Si_{0.50})$	(Al)	(Al)	(Si)	(Si)	(Si)	
O1	$0.247^{\times 2}$	$0.267^{\times 2}$	0.530 ^{×2↓}					$0.912^{\times 2}$	1.956
O2	$0.375^{\times 2}$				$0.452^{\times 2\downarrow}$	$1.079^{\times 2}$			1.906
03	•	$0.420^{\times 2}$		$0.489^{\times 2\downarrow}$			$1.067^{\times 2}$		1.976
04				$0.544^{\times 2\downarrow}$		0.920			2.008
O5		0.124	$0.660^{\times 2\downarrow \rightarrow}$			0.937			2.381
O6					$0.605^{\times 2\downarrow \rightarrow}$				1.210
O7	0.244		$0.714^{\times 2\downarrow \rightarrow}$						1.672
08	0.099				$0.495^{\times 2\downarrow \rightarrow}$		1.093		2.182
O9	0.177						0.932	0.950	2.059
O10		0.425						1.036	1.461
011				$0.581^{\times 2\downarrow}$					1.162
	1.764	1.923	3.808	3.228	3.104	4.015	4.159	3.810	

Table 3. Bond valence sums (v.u.) in the structure of Si-rich Mg-sursassite.





(a)

M3 = 50%AI 50%Si

