1   REVISION 1

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3   Weddellite from renal stones: structure refinement and dependence of crystal chemical

4   features on H_2O content.

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10

11   Abstract

12   The refinement of the structures of 17 weddellite crystals $(Ca(C_2O_4) \cdot (2+x)H_2O$, $I4/m$,

13    $a = 12.329 – 12.378$ Å, $c = 7.345 – 7.366$ Å, $V = 1117.8 – 1128.6$ Å^3) which were taken from the

14   oxalic renal stones of the St. Petersburg (Russian Federation) citizens of both sexes aged from 24

15   to 65 years has been carried out by the means of single crystal X-ray diffraction ($R_1 = 0.024 –$

16   0.057). According to the results of the study, the amount of "zeolitic" water molecules (x) in the

17   structure of weddellite varies from 0.13 to 0.37 p.f.u. A significant positive correlation between

18   the amount of "zeolitic" water in the structure of weddellite and the closest interatomic distance

19   between coordination water molecules in the large channels (OW1–OW1) was found as well as

20   positive correlation between the value of the a parameter and the average distance of <Ca1 – O>

21   in Ca polyhedron. Obtained linear regression equation: $x = 5.43a$ - 66.80, can be used for

22   determination of the "zeolitic" water amount using the known unit cell a parameter with mean-

23   root-square error ±0.03 p.f.u. It was found that the x value for the crystals selected from the

24   "mono-weddellite" stones ($x = 0.13 - 0.24$) are at the bottom of the range, thus we can assume

25   that weddellite crystals with fewer "zeolitic" water amounts would be relatively stable.

26

27   Keywords: Weddellite, calcium oxalate, crystal structure, renal stones, biomineralogy

28

29   Introduction

30   First samples of weddellite $CaC_2O_4 \cdot (2 + x) H_2O$ ($x \leq 0.5$) were found in the sediments of

31 the Weddell Sea (Antarctica) in 1936 (Bannister et al. 1936). The classic form of weddellite

32 crystals is a tetragonal bipyramid, flattened on [001], but sometimes the combination of the

33 tetragonal bipyramid and pinacoid also occurs. Quite often, weddellite dehydrates to more stable

34 whewellite – calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$), forming excellent pseudomorphs of

35 granular whewellite after weddellite tetragonal dipyramids.

36   In nature weddellite occurs in peat and calcareous lake sediments, in biofilms on the

37 surface of limestone, in plants (Graustein et al. 1976, Frank-Kamenetskaya et al. 2012). As well,

38 most part of the human urinary system stones consists of calcium oxalates both mono- and

39 dihydrates (the amount of calcium oxalate stones is up to 75% depending on the region) (Korago

40 1992, Izatulina & Yelnikov 2008). Although the results of thermodynamic calculations show that

41 whewellite is the stable calcium oxalate phase under physiological conditions (Yelnikov et al.

42 2007), the frequency of weddellite occurrence in oxalate uroliths is rather significant. According

43 to our collection (more than 1000 renal stones), 46% of samples contain weddellite, and 5% are

44 mono-weddellite. Quite often a rhythmic alternation of whewellite and weddellite (Fig. 1) is

45 detected in renal stones that indicate a sudden and periodic change in the stone formation

46 conditions.

47   The first data on the crystal structure of weddellite were obtained by Sterling (1965). In

48 course of this study the partially occupied position of "zeolite" water molecules in the structural

49 canals was localized, thus it was shown that the amount of water molecules in the structure of

50 weddellite may vary up to 2.5 molecules per formula unit. Subsequently, Tazzoli and

51 Domenegetti (1980) refined structural data ($x = 0.37$) and revealed a disordered distribution of

52 "zeolitic" water molecules along the z axis (split position of the oxygen atom into two

53   crystallographically independent positions). Based on the results of the structure refinement of

54   the two weddellite crystals from the renal stones (Izatulina & Yelnikov 2008) and the data from

55   Tazzoli and Domenegetti (1980), we have preliminary estimated the range of variation in the

56   amount of water in the structure of weddellite (from 2.13 to 2.37 molecules per formula unit) and

57   a direct relationship between the x value and the value of a unit cell parameter was found at the

58   trends.

59   As the continuation of the research we carried out a representative series of crystal

60   structure investigation experiments to clarify the range of x, to analyze the effect of water

61   amount and its distribution on the geometry of the weddellite structure and to get a regression

62   equation to estimate the amount of water in the structure of weddellite according to the a unit

63   cell parameter.

64

65   Experimental

66   17 isometric colorless transparent crystals were taken from the oxalic renal stones of the

67   St. Petersburg (Russian Federation) citizens of both sexes aged from 24 to 65 years (collection of

68   the Chair of Crystallography, St. Petersburg State University). The stones were removed for

69   medical reasons in various medical institutions of St. Petersburg. To verify the assumption that

70   the amount of "zeolitic" water could be a criterion of weddellite "stability", crystals were

71   selected from the stones of different phase composition, as well as from different zones of a

72   stone. Mineral component of the **1**, **6-8** and **10** sample stones presented mostly by weddellite,

73   whether the other stones contain of whewellite and weddellite mixture in different ratio. In the **3,**

74   **5, 8, 12** and **14** sample stones there are small amounts of hydroxylapatite. The mineral

75   composition of the studied renal stones was determined by the means of powder XRD method

76   using Rigaku Miniflex II diffractometer. Samples were measured at a room temperature using

77   monochromated Cu$K\alpha$ radiation at 30 kV and 15mA in the 2θ range of 10.00–60.00º. Beside the

78   crystals of **3, 12, 14** as well as **7, 10** and **13, 16** were taken from the same renal stones.

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81   Single crystal X-ray analysis

82   The weddellite crystal structure investigations (17 samples) were conducted by the means

83   of single crystal X-ray diffraction analysis using Bruker Smart diffractometer, equipped with the

84   planar type APEX II CCD (charge–coupled device) detector, and STOE IPDS II diffractometer,

85   equipped with a 2-D X-ray sensitive plate with optical memory (Image Plate). Crystals of **1 – 17**

86   were measured at a room temperature using monochromated Mo$K\alpha$ radiation. The unit cell

87   parameters (Table 1) were refined by least square techniques using reflections in the 2θ range of

88   4.00–60.00°. The structures have been solved by the direct methods and refined in the

89   anisotropic approximation of thermal parameters for non hydrogen atoms using SHELX-97

90   program (Sheldrick 2008). Positions of H atoms were localized objectively and refined without

91   restrictions with individual isotropic temperature parameters. For the crystals measured at STOE

92   diffractometer absorption correction was introduced using X-RED program by numerical

93   integration taking into account the experimentally determined and optimized crystal shape by X-

94   SHAPE algorithm (Stoe & Cie 2005). For the crystals measured at Bruker diffractometer

95   absorbance correction was applied using SADABS program (Sheldrick 2004). Selected bond

96   lengths and angles for **1 – 17** are listed in Tables 2-4. Atomic coordinates and displacement

97   parameters for all atoms in the structures of **1 – 17** as well as other crystallographic data are on

98   deposit provided as a CIF.

99

100   Results and discussion

101   Structure description

102   Calcium oxalate dihydrate crystallizes in tetragonal $I4/m$ space group. The main

103   "building" block of the weddellite structure (Fig. 2) is the Ca-polyhedra - slightly distorted

104   square antiprism. There is one crystallographically independent Ca atom in the structure that

105   form eight bonds with oxygen atoms (Table 2): six O atoms belong to four equivalent oxalate

106   groups (four bonds with O1 and two with O2 atoms) and two more water molecules (OW1 and

107   OW2). Each Ca polyhedron share common O1 – O1 edges with two neighbor polyhedra to form

108   infinite chains of square antiprisms arranged along the [001] direction. These chains connected

109   with each other via … C_2O_4 – H_2O – C_2O_4 … complexes arranged parallel to (100) plane (Fig.

110   3). The oxalate groups and water molecules of the complexes connected by hydrogen bonding

111   OW1 – H1 ⋯ O2 and OW2 – H2 ⋯ O2 (Table 3).

112   Rotation of Ca polyhedra chains and water – oxalate complexes around the fourfold axis

113   results in formation of two types of channels in the structure of weddellite arranged along the c

114   axis and differ in internal diameter. The walls of the larger channels passing through the origin

115   and center of the unit cell, formed by water molecules OW1 (four OW1 molecules arranged in

116   the plane parallel to (001) to form a regular square with an edge OW1 – OW1 ~ 3.2 Å and

117   diagonal distance ~ 4.6 Å). At the center of the large channels there are "zeolitic" water

118   molecules arranged on the fourfold axis, the position of the oxygen atom of which are split into

119   two independent similar and substantially vacant positions (OW3 and OW31), separated by a

120   distance ~ 0.6 Å. The hydrogen atoms of the "zeolitic" water molecules were not localized at the

121   difference Fourier synthesis which allows us to suggest that the protons are distributed

122   statistically. Large channels filled with "zeolitic" water, alternate with empty channels of smaller

123   diameter, which pass through the center of the unit cell edges parallel to the a and b axes. The

124   diameter of the channel (~ 3.0 Å) determined by the distance between the OW2 molecules

125   localized in it.

126   C1 – C1 bond length in the oxalate groups arranged along the c axis, vary from 1.549 to

127   1.557 Å, and the average bond length <C1 – O> are in the range of 1.245 – 1.250 Å (Table 4).

128   The distance between the oxygen atoms of the "zeolitic" water (OW3 and OW31) and

129   oxygen atoms OW1 located in the same channel (~ 3.5-3.1 Å) are close to the distance OW1-

130   OW1 (~ 3.2-3.3 Å), thus it could be described as the presence of slightly distorted octahedral

131   groups (with the bases formed by OW1 atoms, and apical vertices by OW3/OW31) as well as the

132   square complexes of oxygen OW1 atoms in the large channels. The OW3 – OW1 distance (~ 3.5

133   Å) is significantly longer than the distance OW31 –OW1 (3.1 Å) presumably because the

134   structure tend to implement sustainable clusters of water molecules due to the "zeolitic" water

135   position splitting (the appearance of OW31 position). The presence of a prohibited distance

136   between oxygen atoms OW3, linked through the inversion center (1.9 - 2.2 Å), indicate that the

137   centrosymmetricity of the weddellite structure realizes only statistically.

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139   Effect of "zeolitic" water amount variation on the geometry of the weddellite structure

140   As the amount of "zeolitic" water molecules in the structure of weddellite increases the

141   value of $(OW1)_4 : (OW1)_4(OW3/OW31)_2$ ratio decreases from ~ 7 to ~ 2, according to the ratio

142   of the respective positions occupation. There is a significant positive correlation (Fig. 4) between

143   the amount of "zeolitic" water in the structure of weddellite ($x = 0.13 – 0.37$ p.f.u.) and the

144   closest interatomic distance OW1–OW1 = 3.211 - 3.279 Å (edge of the OW1-based square

145   complex).

146   The displacement of the oxygen OW1 atoms (Fig. 5), arranged in the plane of symmetry,

147   with the increase of x values, leads to changes in other interatomic distances. The average

148   distance <Ca1 – O> varies from 2.453 to 2.460 Å with the increase of x. The shortest bond

149   length with OW1 oxygen atoms vary from 2.390 to 2.395 Å. Longer bond length with the OW2

150   atoms vary from 2.445 to 2.457 Å. Bond lengths with oxygen atoms of oxalate groups fall in the

151   range: Ca1 – O1 = 2.453 – 2.463 Å and 2.494 – 2.506 Å; Ca1 – O2 = 2.445 – 2.449 Å.

152   Changes in the interatomic distances and, especially, the increase in the bond lengths in

153   the (001) plane, leads to significant variations in the values of the unit cell parameters (Table 1).

154   The a parameter increases significantly than others (from 12.329 to 12.378 Å) and considerable

155   positive correlation observed between the value of the a parameter and the occupancy of

156   "zeolitic" water positions (Fig. 6). Obtained linear regression equation: $x = 5.43a$ - 66.80, can be

157   used for determination of the "zeolitic" water amount (x) using the known unit cell a parameter

158   with mean-root-square error ±0.03 p.f.u (if standard error of a parameter determination ≤ 0.001

159   Å). A significant positive correlation is also observed between the value of the a parameter and

160   the average distance of <Ca1 – O> (Fig. 7), which is well explained by the changes in the Ca-

161   polyhedron bond lengths with an increase of the amount of "zeolitic" water in the structure, that

162   is discussed above. The c unit cell parameter in the structures fall in the range of 7.345-7.366 Å,

163   but the regular changes of this parameter with the amount of "zeolitic" water have not been

164   identified.

165   Thus, the crystal structures of 17 weddellite crystals $CaC_2O_4 \cdot (2 + x)\,H_2O$ which were

166   taken from the oxalic renal stones of the St. Petersburg (Russian Federation) citizens of both

167   sexes aged from 24 to 65 years were refined to $R_1 = 0.024 – 0.057$. According to the results of

168   the study and the available literature data, the amount of "zeolitic" water molecules (x) in the

169   structure of weddellite varies from 0.13 to 0.37 p.f.u. As the number of "zeolitic" water

170   molecules in the structure increase, the amount of octahedral water complexes and the size of the

171   calcium polyhedra increase too. Channels along the c axis expand and unit cell parameters

172   increase with the growth of x value as well.

173   An interesting result is that the x value for the crystals from "mono-weddellite" stones

174   fall in the range of $0.13 – 0.24$ p.f.u. In the recent paper Conti et al. 2010 suggests that there is a

175   range of water whereby weddellite crystals are stable, while the increase and decrease of the

176   water amount leads to the destruction of crystals. It is also known (Frank-Kamenetskaya et al.

177   2012) that for the weddellite crystals formed by the influence of microscopic fungi (*Aspergillus

178   niger* strain, active producer of organic acids) $x = 0.10 - 0.24$. Such weddellite could be

179   considered relatively stable, since it is stored in the dried sludge. Whereas crystals obtained in

180   our experiments, transforms to whewellite after drying the precipitate. The x value determined

181   for the weddellite crystals obtained in the presence of bacteria and viruses from the equation

182   suggested above varies from 0.21 to 0.28 p.f.u. Thus perhaps the weddellite in oxalate renal

183   stones (Fig. 1), substituted for calcium oxalate monohydrate, was formed during inflammatory

184   processes.

Implications

186   Calcium oxalates are one of the most common pathogenic entities. They are the part of

187   humans, cats and dogs kidney stones, and also found in pathogenic entities in the human lungs.

188   Along with stable calcium oxalate monohydrate, such entities often contain metastable

189   weddellite. Being in the body and during subsequent retrieval the bipyramidal weddellite crystals

190   injure living tissues. Low concentrations of various impurities among the factors that change the

191   stability of weddellite, which themselves or indirectly through the entry of water into the

192   structure during the calcium oxalate crystallization, could strongly shift the phase equilibrium,

193   change the crystallization kinetics and, therefore, significantly affect the formation of calcium

194   oxalates in the human body. Thus, the study of weddellite crystal structure and its stability under

195   different conditions should expand the knowledge on pathogenic crystal growth processes in

196   living organisms and the development of the theory of oxalate stone formation in humans and

197   animals. Such studies are considered as the building blocks underlying the biomolecular

198   technologies for prevention and treatment of diseases associated with lithiasis.

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Acknowledgments

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236   weddellite: re-examination and comparison. American Mineralogist, 65, 327-334.

237 Table 1. Crystallographic data and refinement parameters for the examined weddellite crystal structures (**1 – 17**). Space group $I4/m$, $Z=8$, Mo$K\alpha$.
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Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
a (Å)	12.3363(13)	12.3543(13)	12.3462(11)	12.3530(5)	12.3528(5)	12.3542(5)	12.3565(5)	12.3443(14)	12.3573(6)
c (Å)	7.3448(8)	7.3547(9)	7.3535(7)	7.3594(3)	7.3569(3)	7.3604(3)	7.3592(3)	7.3599(8)	12.3573(6)
V (Å^3)	1117.8(2)	1122.5(2)	1120.88(18)	1123.02(8)	1122.60(8)	1123.39(8)	1123.63(8)	1121.5(2)	1123.69(10)
μ (mm^{-1})	1.084	1.081	1.083	1.081	1.081	1.080	1.080	1.082	1.081
D_{calc} (g/cm^3)	1.976	1.980	1.982	1.980	1.980	1.978	1.979	1.983	1.984
Diffractometer	Stoe IPDS II	Stoe IPDS II	Stoe IPDS II	Bruker Smart Apex II	Bruker Smart Apex II	Bruker Smart Apex II	Bruker Smart Apex II	Stoe IPDS II	Bruker Smart Apex II
Crystal size (mm^3)	0.32×0.21 ×0.18	0.30×0.24 ×0.19	0.28×0.22 ×0.16	0.24×0.18 ×0.16	0.22×0.15 ×0.13	0.23×0.19 ×0.16	0.21×0.17 ×0.12	0.35×0.27 ×0.21	0.25×0.22 ×0.17
Total reflections with $I > 2\sigma(I)$	6579	6502	6609	7554	8769	7504	5051	5254	8596
Unique reflections	1026	1030	1032	885	1081	885	885	815	1081
Angle range 2θ, º	4.66–63.90	6.44–63.80	4.66–63.82	4.66–59.96	4.66–64.86	4.66–59.96	4.66–59.96	4.66–58.72	4.66–62.84
Reflections with $|F_o| \geq 4\sigma_F$	834	901	909	778	974	791	756	646	913
R_{int}	0.0557	0.0501	0.0433	0.0287	0.0280	0.0267	0.0350	0.0502	0.0351
R_σ	0.0328	0.0251	0.0222	0.0172	0.0154	0.0147	0.0246	0.0336	0.0223
R_1 ($|F_o| \geq 4\sigma_F$)	0.0471	0.0519	0.0435	0.0259	0.0250	0.0248	0.0271	0.0344	0.0259
wR_2 ($|F_o| \geq 4\sigma_F$)	0.0842	0.0924	0.0782	0.0751	0.0661	0.0724	0.0752	0.0643	0.0684
R_1 (all data)	0.0661	0.0629	0.0538	0.0295	0.0283	0.0279	0.0324	0.0543	0.0321
wR_2 (all data)	0.0895	0.0966	0.0818	0.0769	0.0680	0.0740	0.0777	0.0690	0.0713
S	1.101	1.093	1.085	1.061	1.076	1.062	0.997	1.011	1.077
ρ_{min}, ρ_{max}, e/Å^3	–0.535, 0.500	–0.581, 0.507	–0.397, 0.491	–0.364, 0.377	–0.276, 0.531	–0.397, 0.426	–0.358, 0.429	–0.422, 0.460	–0.297, 0.492

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

240   Table 1. Continue.
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Sample	10	11	12	13	14	15	16	17
a (Å)	12.3558(7)	12.3576(8)	12.3567(6)	12.3530(5)	12.363(2)	12.3620(5)	12.3627(6)	12.3783(8)
c (Å)	7.3601(4)	7.3578(5)	7.3573(3)	7.3603(3)	7.3460(17)	7.3574(3)	7.3574(3)	7.3659(5)
V (Å^3)	1123.64(11)	1123.61(13)	1123.37(9)	1124.83(7)	1122.7(4)	1124.35(8)	1124.48(9)	1128.62(13)
μ (mm^{-1})	1.080	1.081	1.082	1.080	1.082	1.081	1.081	1.079
D_{calc} (g/cm^3)	1.978	1.980	1.991	1.988	1.992	1.991	1.994	1.997
Diffractometer	Bruker Smart Apex II	Bruker Smart Apex II	Bruker Smart Apex II	Bruker Smart Apex II	Stoe IPDS II	Bruker Smart Apex II	Bruker Smart Apex II	Bruker Smart Apex II
Crystal size (mm^3)	0.29×0.21 ×0.15	0.21×0.18 ×0.15	0.28×0.22 ×0.16	0.29×0.22 ×0.18	0.33×0.29 ×0.21	0.24×0.20 ×0.16	0.34×0.31 ×0.22	0.32×0.24 ×0.19
Total reflections with $I > 2\sigma(I)$	7511	4960	5508	5844	5150	5046	5070	5039
Unique reflections	885	885	885	1082	815	887	887	891
Angle range 2θ, °	4.66–59.96	4.66–59.98	4.66–59.98	4.66–59.96	6.44–58.62	4.66–59.98	4.66–59.98	4.66–60.00
Reflections with $|F_o| \geq 4\sigma_F$	825	754	812	976	683	772	774	767
R_{int}	0.0252	0.0273	0.0262	0.0222	0.0754	0.0259	0.0277	0.0302
R_σ	0.0116	0.0202	0.0147	0.0158	0.0419	0.0199	0.0207	0.0224
R_1 ($|F_o| \geq 4\sigma_F$)	0.0240	0.0242	0.0240	0.0259	0.0415	0.0256	0.0256	0.0251
wR_2 ($|F_o| \geq 4\sigma_F$)	0.0659	0.0651	0.0651	0.0722	0.0769	0.0717	0.0712	0.0664
R_1 (all data)	0.0256	0.0297	0.0263	0.0295	0.0568	0.0299	0.0300	0.0304
wR_2 (all data)	0.0670	0.0672	0.0664	0.0757	0.0815	0.0739	0.0734	0.0691
S	1.070	1.092	1.119	0.996	1.106	1.063	1.073	1.076
ρ_{min}, ρ_{max}, e/Å^3	−0.250, 0.485	−0.285, 0.387	−0.226, 0.425	−0.290, 0.508	−0.424, 0.366	−0.245, 0.525	−0.309, 0.452	−0.333, 0.404

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

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268 Table 2. Calcium atom polyhedron: bond lengths (Å) for **1** – **17**.

Sample	Ca1 – OW1	Ca1 – OW2	Ca1 – O2 x2	Ca1 – O1 x2	Ca1 – O1 x2	<Ca1 – O>
1 $x = 0.133$	2.392(3)	2.448(3)	2.4449(18)	2.4528(16)	2.4945(15)	2.453
2 $x = 0.190$	2.391(3)	2.454(3)	2.4455(19)	2.4576(17)	2.4994(16)	2.457
3 $x = 0.192$	2.391(3)	2.449(3)	2.4453(16)	2.4568(14)	2.4977(13)	2.455
4 $x = 0.192$	2.3942(16)	2.4479(17)	2.4488(11)	2.4583(9)	2.5022(9)	2.458
5 $x = 0.197$	2.3937(14)	2.4498(15)	2.4470(9)	2.4588(8)	2.4985(8)	2.457
6 $x = 0.199$	2.3950(15)	2.4486(16)	2.4486(10)	2.4592(9)	2.5013(9)	2.458
7 $x = 0.199$	2.3932(17)	2.4489(18)	2.4486(11)	2.4598(10)	2.5017(9)	2.458
8 $x = 0.213$	2.390(2)	2.446(3)	2.4461(16)	2.4571(14)	2.5010(13)	2.456
9 $x = 0.230$	2.3933(15)	2.4494(16)	2.4473(10)	2.4603(9)	2.5010(9)	2.457
10 $x = 0.237$	2.3941(15)	2.4492(16)	2.4479(10)	2.4594(9)	2.5010(9)	2.457
11 $x = 0.257$	2.3930(16)	2.4495(17)	2.4469(10)	2.4607(9)	2.5006(9)	2.457
12 $x = 0.257$	2.3915(15)	2.4506(16)	2.4468(10)	2.4593(9)	2.5001(9)	2.457
13 $x = 0.262$	2.3951(15)	2.4522(16)	2.4477(10)	2.4604(8)	2.5016(8)	2.458
14 $x = 0.267$	2.394(3)	2.452(3)	2.4450(18)	2.4568(16)	2.4970(15)	2.455
15 $x = 0.275$	2.3933(17)	2.4469(11)	2.4510(18)	2.4608(10)	2.5004(9)	2.458
16 $x = 0.289$	2.3920(16)	2.4510(17)	2.4465(11)	2.4601(9)	2.5021(9)	2.458
17 $x = 0.347$	2.3949(16)	2.4539(17)	2.4475(10)	2.4636(9)	2.5056(9)	2.460

269   Table 3. Oxalic group: bond lengths (Å) and angles (°) for **1 – 17**.

Sample	C1 – O1 x2	C1 – O2 x2	<C1 – O>	O2 – C1 – O1	O2 – C1 – C1	O1 – C1 – C1	O1 – C1 – C1
1 $x = 0.133$	1.251(2)	1.244(3)	1.248	126.9(2)	116.10(12)	116.96(12)	1.549(4)
2 $x = 0.190$	1.252(3)	1.247(3)	1.249	126.7(2)	116.18(13)	117.07(12)	1.548(4)
3 $x = 0.192$	1.251(2)	1.245(2)	1.248	126.79(17)	116.10(11)	117.09(10)	1.549(3)
4 $x = 0.192$	2.3947(15)	2.3810(17)	1.248	126.84(13)	116.15(8)	117.00(7)	1.553(3)
5 $x = 0.197$	1.2524(12)	1.2474(13)	1.25	126.75(11)	116.17(7)	117.06(6)	1.552(2)
6 $x = 0.199$	1.2495(14)	1.2473(14)	1.248	126.79(12)	116.13(7)	117.06(7)	1.552(2)
7 $x = 0.199$	1.2482(16)	1.552(3)	1.248	126.71(13)	116.14(8)	117.12(8)	1.2471(16)
8 $x = 0.213$	1.249(2)	1.242(2)	1.246	127.03(17)	116.00(11)	116.96(10)	1.557(4)
9 $x = 0.230$	1.2498(13)	1.2469(14)	1.248	126.72(12)	116.12(7)	117.14(7)	1.550(2)
10 $x = 0.237$	1.2504(13)	1.2468(14)	1.249	126.85(12)	116.11(7)	117.02(7)	1.554(2)
11 $x = 0.257$	1.2489(15)	1.2478(15)	1.248	126.66(12)	116.12(8)	117.20(7)	1.549(3)
12 $x = 0.257$	1.2513(14)	1.2473(14)	1.249	126.71(12)	116.19(7)	117.09(7)	1.551(2)
13 $x = 0.262$	1.2516(13)	1.2472(13)	1.249	126.68(11)	116.19(7)	117.11(6)	1.550(2)
14 $x = 0.267$	1.252(3)	1.244(3)	1.248	127.15(18)	115.94(12)	116.89(11)	1.552(4)
15 $x = 0.275$	1.2505(15)	1.2462(15)	1.248	126.79(13)	116.09(8)	117.11(7)	1.552(3)
16 $x = 0.289$	1.2485(15)	1.2475(15)	1.248	126.87(13)	116.05(8)	117.07(7)	1.552(3)
17 $x = 0.347$	1.2506(15)	1.2481(15)	1.249	126.71(13)	116.10(8)	117.18(7)	1.550(3)

270   Table 4. Hydrogen bonds and other water intermolecule parameters: bond lengths (Å) and angles (°) for **1 – 17**.

Sample	OW1 – O2	OW1 – H1 x2	H1 – O2	OW1 – H1 – O2	OW2 – O2	OW2 – H2 x2	H2 – O2	OW2 – H2 – O2	OW3 – OW31	OW3 – OW3	OW3 – O2 x4	OW3 – OW1 x4	OW31 – OW31	OW31 – O2 x4	OW31 – OW1 x4
1 x = 0.133	2.922(3)	0.90(5)	2.067	158.2	2.863(3)	0.80(6)	2.255	133.4	0.60(19)	2.0(6)	3.28(3)	3.5(2)	3.2(3)	3.280(12)	3.08(9)
2 x = 0.190	2.925(3)	0.87(5)	2.104	155.9	2.862(3)	0.84(6)	2.129	145.8	0.62(9)	2.0(3)	3.301(15)	3.54(10)	3.21(15)	3.295(7)	3.09(5)
3 x = 0.192	2.924(2)	0.89(4)	2.094	155.0	2.862(3)	0.76(6)	2.365	124.1	0.54(11)	2.2(4)	3.284(13)	3.44(15)	3.3(2)	3.293(11)	3.06(7)
4 x = 0.192	2.9232(16)	0.924(18)	2.121	144.6	2.8653(17)	0.926(18)	2.218	126.3	0.61(4)	2.19(16)	3.282(6)	3.45(6)	3.42(14)	3.297(8)	3.02(4)
5 x = 0.197	2.9206(14)	0.928(17)	2.094	147.6	2.8626(15)	0.937(18)	2.172	129.7	0.56(3)	2.33(13)	3.282(3)	3.40(5)	3.45(12)	3.302(7)	3.01(4)
6 x = 0.199	2.9233(15)	0.921(18)	2.123	144.6	2.8660(16)	0.932(18)	2.214	126.3	0.59(3)	2.26(14)	3.280(4)	3.43(5)	3.44(13)	3.298(8)	3.01(4)
7 x = 0.199	2.9221(17)	0.920(18)	2.117	145.5	2.8653(17)	0.936(18)	2.145	132.9	0.61(5)	2.06(18)	3.293(8)	3.50(7)	3.29(9)	3.296(5)	3.29(9)
8 x = 0.213	2.928(2)	0.84(3)	2.141	155.3	2.867(2)	0.72(5)	2.376	127.0	0.57(14)	2.1(4)	3.290(19)	3.50(16)	3.10(5)	3.288(7)	3.19(16)
9 x = 0.230	2.9224(15)	0.907(17)	2.125	146.2	2.8653(16)	0.920(18)	2.137	135.3	0.62(3)	2.16(13)	3.289(5)	3.47(5)	3.39(9)	3.301(5)	3.03(3)
10 x = 0.237	2.9228(15)	0.926(17)	2.088	149.2	2.8647(16)	0.937(18)	2.179	129.2	0.59(4)	2.22(15)	3.284(5)	3.44(6)	3.03(4)	3.298(7)	3.40(13)
11 x = 0.257	2.9204(16)	0.907(17)	2.112	148.0	2.8656(16)	0.925(18)	2.138	134.8	0.61(3)	2.22(12)	3.288(4)	3.45(4)	3.43(9)	3.305(5)	3.02(3)
12 x = 0.257	2.9198(15)	0.920(18)	2.089	149.6	2.8609(16)	0.931(18)	2.173	129.9	0.60(3)	2.17(13)	3.293(5)	3.47(5)	3.36(8)	3.303(5)	3.05(3)
13 x = 0.262	2.9195(15)	0.932(18)	2.072	150.6	2.8613(16)	0.937(19)	2.23	124.0	0.58(3)	2.27(11)	3.291(3)	3.43(4)	3.44(9)	3.309(6)	3.02(3)
14 x = 0.267	2.922(3)	0.84(4)	2.114	161.0	2.865(3)	0.83(4)	2.117	149.5	0.66(8)	1.9(2)	3.306(12)	3.56(8)	3.25(9)	3.301(5)	3.08(3)
15 x = 0.275	2.9197(16)	0.933(18)	2.051	154.4	2.8621(17)	0.942(19)	2.183	128.2	0.59(3)	2.29(11)	3.291(3)	3.42(4)	3.48(9)	3.313(6)	3.01(3)
16 x = 0.289	2.9198(16)	0.925(18)	2.09	148.6	2.8634(17)	0.928(18)	2.145	133.5	0.60(3)	2.18(13)	3.296(5)	3.47(5)	3.37(8)	3.307(5)	3.05(3)
17 x = 0.347	2.9217(16)	0.906(17)	2.125	146.3	2.8642(16)	0.929(18)	2.092	139.8	0.61(3)	2.13(10)	3.309(4)	3.50(4)	3.34(6)	3.318(3)	3.07(2)
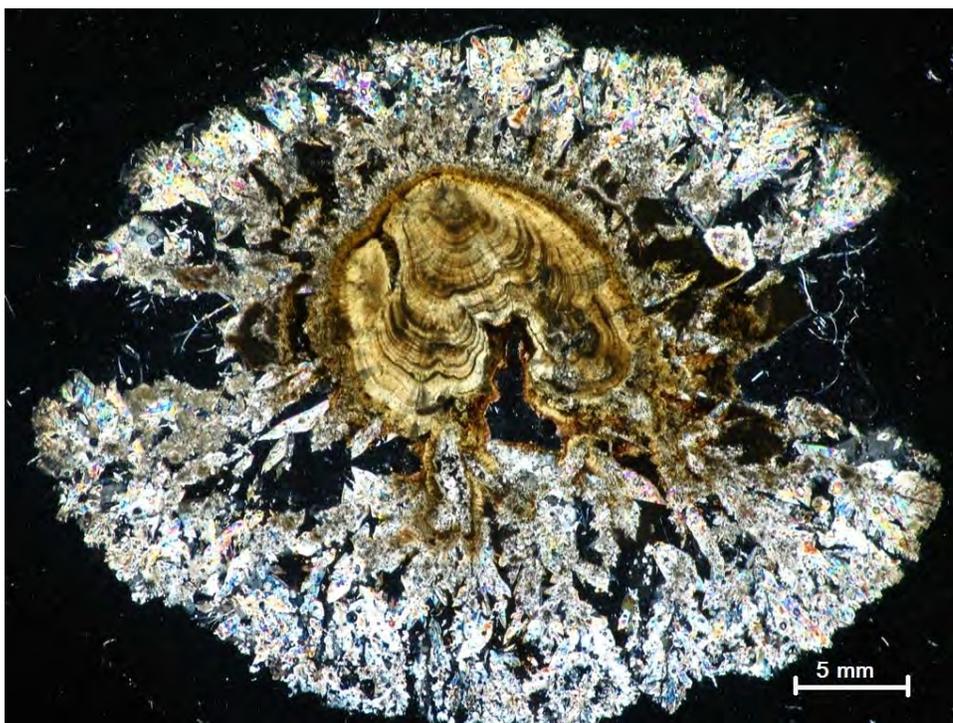
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273 Figure 1. Biomineral renal stone: central part – whewellite, outer part – weddelite. Picture taken
274 in polarized light.
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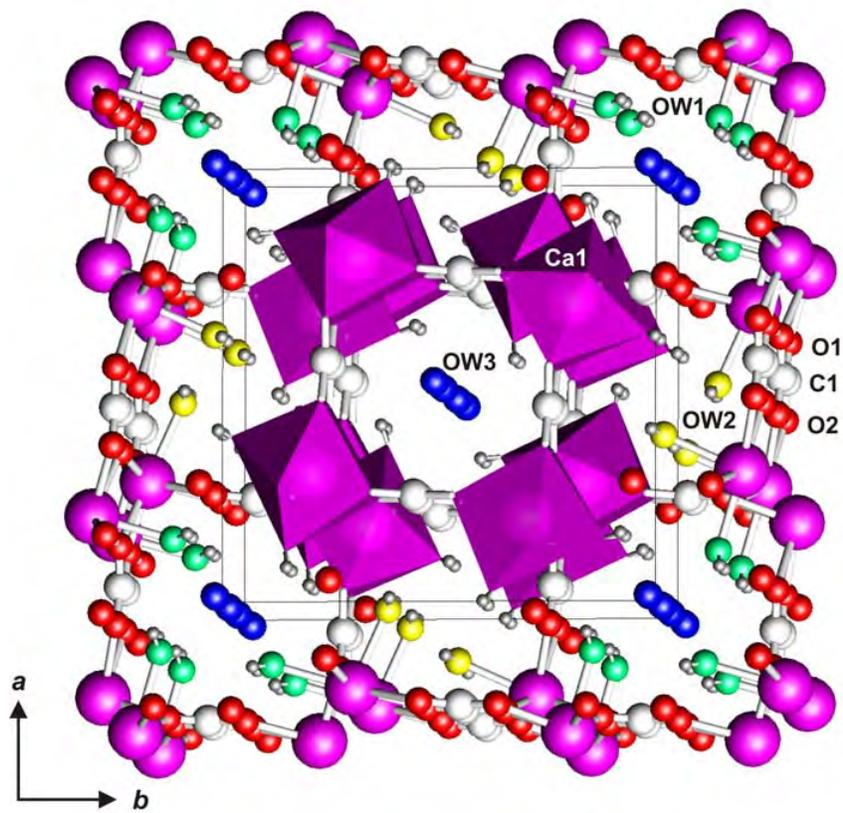
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280   Figure 2. Crystal structure of weddellite; section almost parallel to (001).
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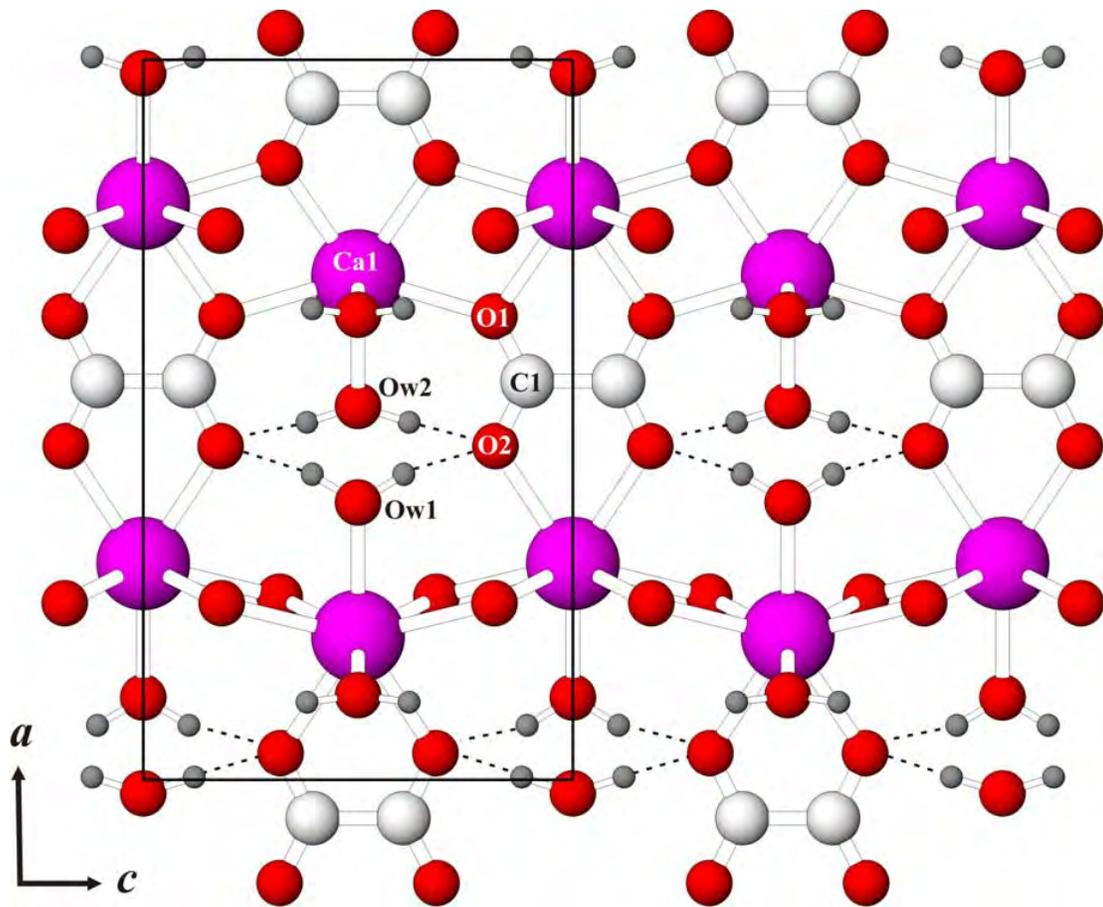
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284   Figure 3. Crystal structure of weddellite; section parallel to (010).
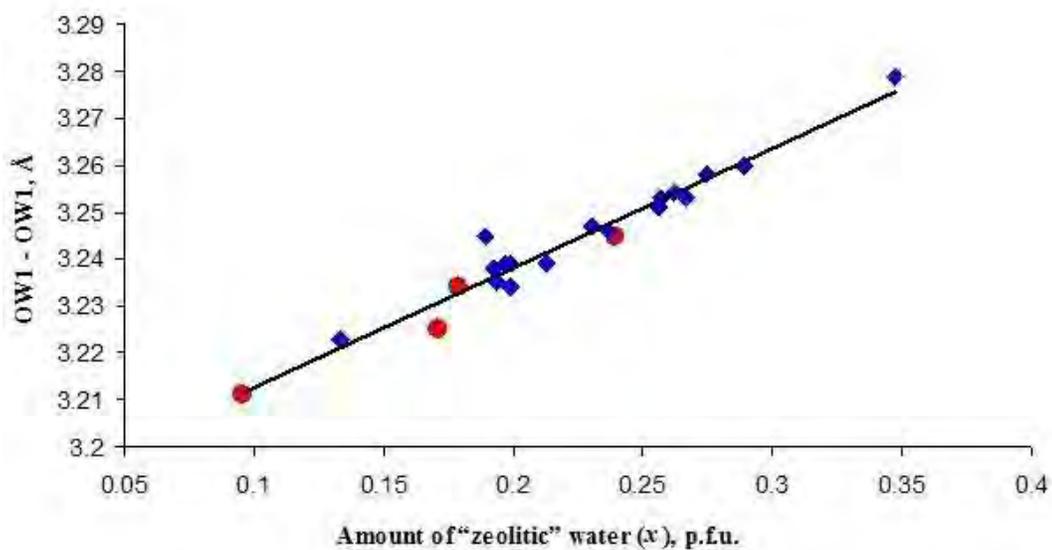
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287   Figure 4. Correlation of OW1 – OW1 distance with amount of "zeolitic" water molecules;
288   rhombuses – this work, circles – Rusakov et al. (unpublished data).

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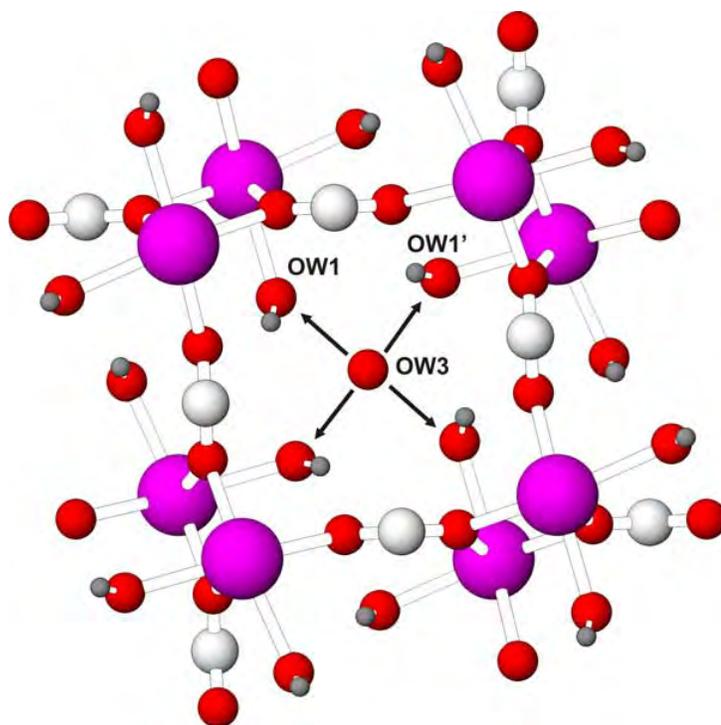
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291
292   Figure 5. Part of the weddellite structure parallel to (001): displacement of the OW1 atoms with
293   the increase of x.
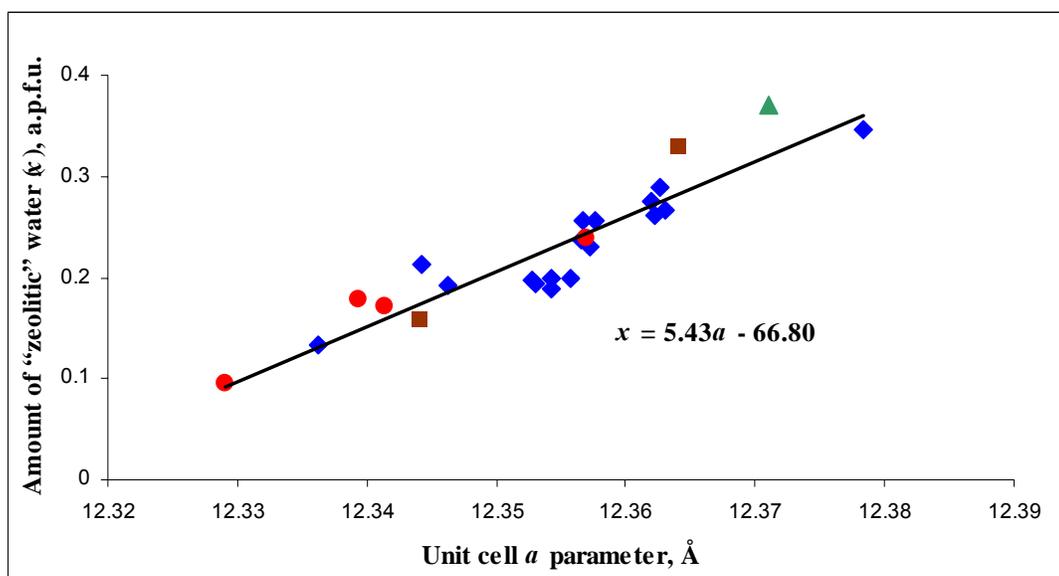
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296   Figure 6. Correlation of unit cell *a* parameter with amount of "zeolitic" water molecules;
297   rhombuses – this work, circles – Rusakov et al. (unpublished data), squares – Izatulina &
298   Yelnikov 2008, triangular – Tazzoli & Domeneghetti 1980.
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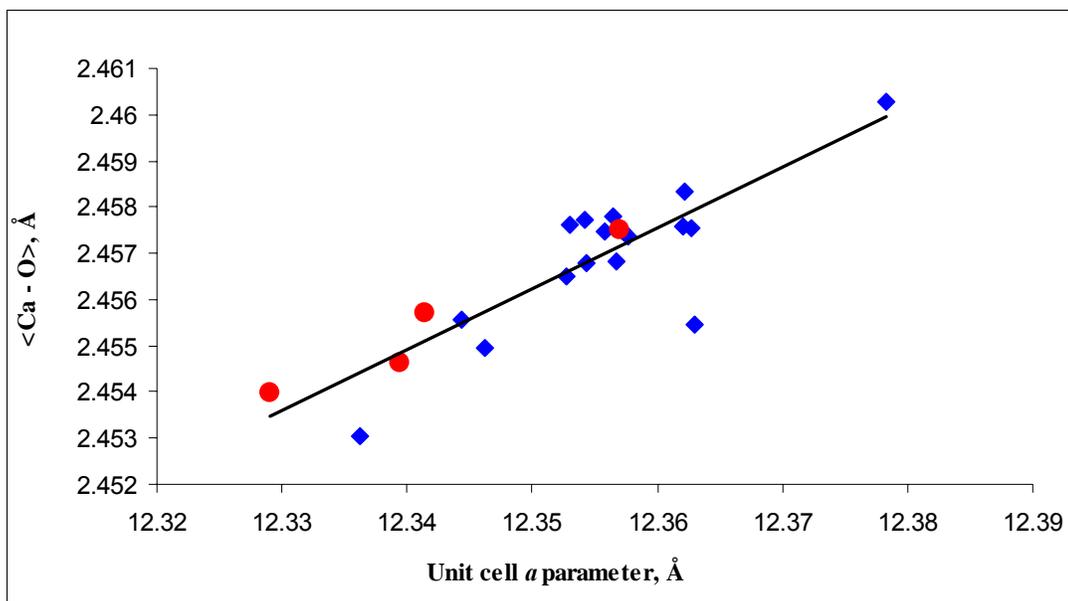
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302 Figure 7. Correlation of <Ca – O> distance in Ca polyhedron with amount of "zeolitic" water
303 molecules; rhombuses – this work, circles – Rusakov et al. (unpublished data).
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