Acidities of MgO Surface Sites: Implication for the Formation Mechanism of $Mg(OH)_2$

Sai Adapa[1], Ke Yuan[1], Barbara R Evans[1], Stephan Irle[2], Juliane Weber[1], Lawrence M Anovitz[1], Andrew G Stack[1*]

*Corresponding email: stackag@ornl.gov

[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[2]Computational Sciences & Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Supporting information

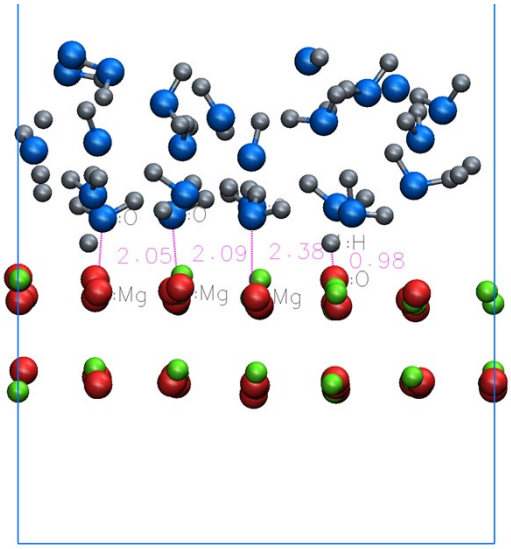

Figure S1: Schematic of equilibrated MgO(100)-water interface. Distances between surface Mg and respective terminal water molecules (~2.16 Å) and surface O_s and respective hydroxylating H^+ ions (~0.98 Å) are showed as dotted lines. Note that schematic is showing sub-surface, surface and two layers thickness of water molecules.

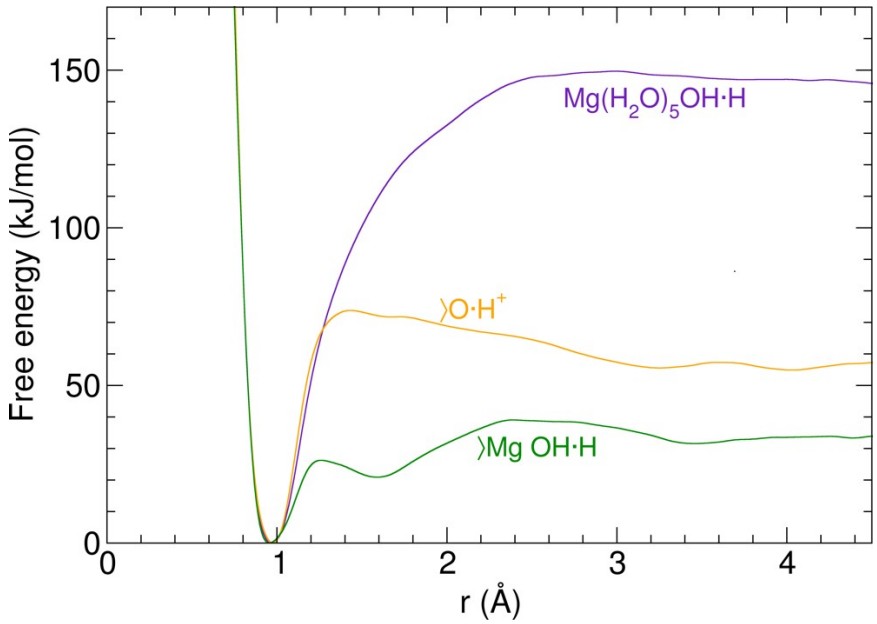

Figure S2: Free energy profiles of deprotonation of the aqueous Mg^{2+} ion, the surface bridging oxygen hydroxyl and the terminal water of exposed Mg^{2+} ion up to separation distance of 4.5 Å

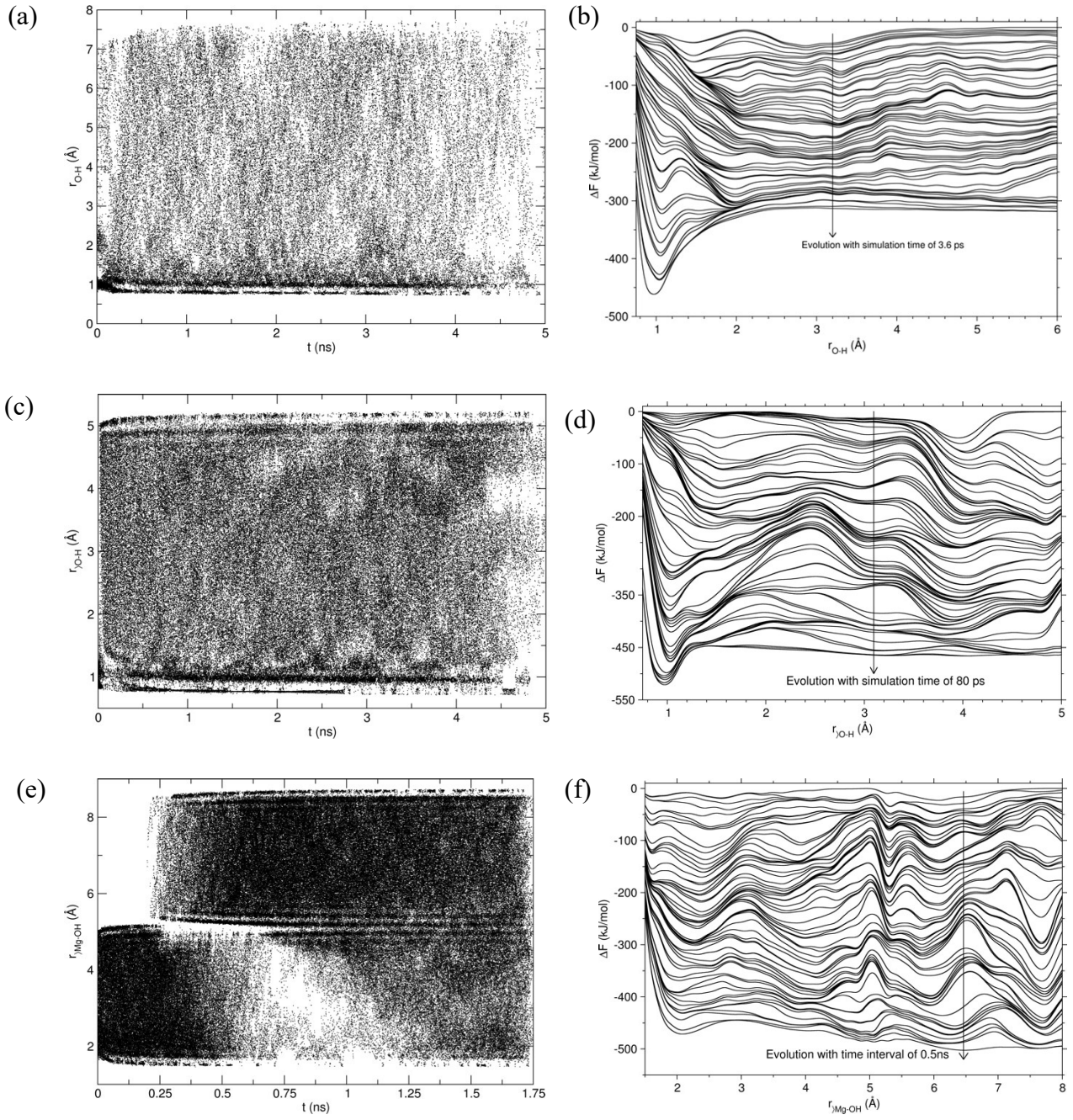

Figure S3: Evolution of collective variable in state space and free energy profiles of deprotonation of ((a) and (b)) aqueous Mg^{2+} ion ((c) and (d)) the surface bridging oxygen hydroxyl, and ((e) and (f)) aqueous OH^- adsorption.

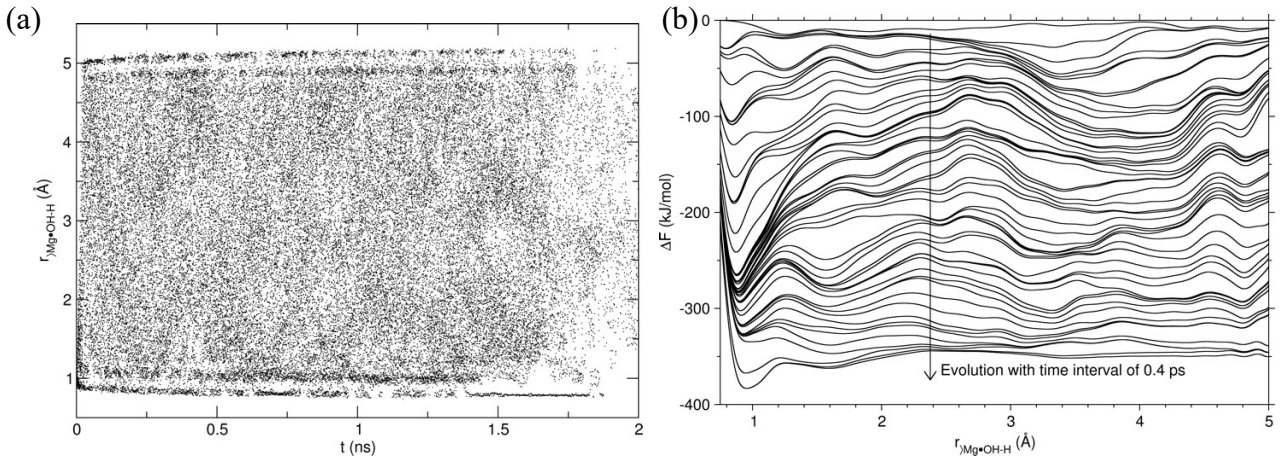

Figure S4: Evolution of (a) collective variable in state space and (b) free energy profiles of terminal water deprotonation with simulation time.

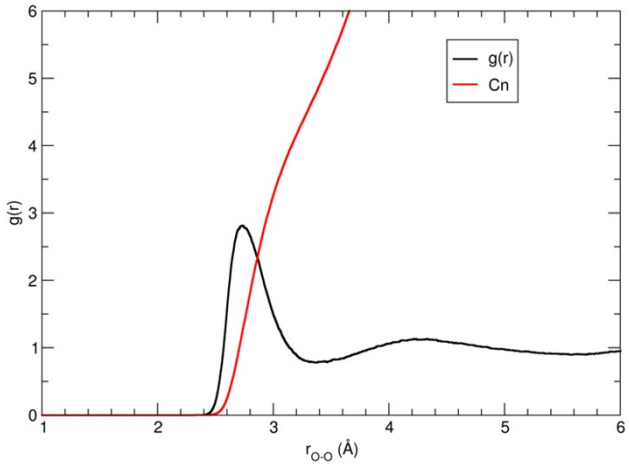

Figure S5: Pair correlation and coordination number of oxygen atoms of water molecules in aqueous Mg^{2+} system.

Attraction energy between $OH^- - H_3O^+$ pair (columbic) :

$$E_c = -\frac{1}{4\pi\varepsilon_r\varepsilon_o} * \frac{-1e * 1e}{r}$$

where $\varepsilon_r = 78$ is relative permittivity of water; $\varepsilon_o = 8.854188 * 10^{-12}\ C^2N^{-1}m^{-2}$ is vacuum permittivity; e = $1.602177 * 10^{-19}\ C$ is charge; r = 2.73 Å is location of maximum in $g(r)_{O\text{-}O}$; N_A is Avogadro's number.

$$E_c = 2.69060944\ k_BT = 1.16850927\ pK_a$$

PHREEQC aqueous speciation WATEQ4F model:

Case: Hydration of MgO in water. Surface sites are in equilibrium, but dissolution is restricted

Input file:

```
database wateq4f.dat
SURFACE_MASTER_SPECIES
      Mgo_s  Mgo_sO
      Mgo_w  Mgo_wOH2

SURFACE_SPECIES
      Mgo_sO = Mgo_sO
      log_k  0.0

      Mgo_wOH2 = Mgo_wOH2
      log_k  0.0

      Mgo_sO  + H+ = Mgo_sOH+
      log_k  13.5   # = pKa1,int

      Mgo_wOH2 = Mgo_wOH- + H+
      log_k  -5.5   # = pKa2,int

solution 1
SURFACE 1
# surface             sites in moles       surf. area (m^2/g)  g/L
     Mgo_s       2e-5     32.20      4
     Mgo_w       2e-5
EQUILIBRIUM_PHASES
#           periclase 0.0
#           CO2(g) -3.37
PHASES

# References
#
```

```
# A. L. Harrison, V. Mavromatis, E. H. Oelkers and P. Bénézeth Solubility of the Hydrated Mg-Carbonates
#Nesquehonite and Dypingite from 5 to 35 °C:
#  Implications for CO2 Storage and the Relative Stability of Mg-Carbonates, Chem. Geol., 2019, 504, 123-135,
#DOI: 10.1016 j.chemgeo.2018.11.003.

# R. J. Hill, J. H. Canterford and F. J. Moyle, New Data for Lansfordite, Mineral. Mag., 1982, 46(341), 453-457,
#DOI: 10.1180/minmag.1982.046.341.08.

# W. Hummel, U. Berner, E. Curti, F. J. Pearson and T. Thoenen, Nagra/PSI Chemical Thermodynamic Data Base
#01/01, Radiochim. Acta, 2002, 90(9-11), 805-813, DOI: 10.1524/ract.2002.90.9-11_2002.805.

# H. S. Santos; H. Nguyen; F. Venâncio, D. Ramteke, R. Zvenhoven, P. Kunnunen (2023) Mechanisms of Mg
# carbonates precipitation and implications for CO2  capture and utilization/ storage.  Inorg. Chem. Front.   DOI:
#10.1039/d2qi02482a

Nesquehonite        149
      MgCO3:3H2O = Mg+2 + CO3-2 + 3H2O
      log_k          -5.27    #  Santos, 2023; originally from Harrison et al., 2019
      delta_h -5.789 kcal

Magnesite
      MgCO3 = Mg+2 + CO3-2
      log_k          -8.029   # Santos, 2023.  wateq4f.dat uses -8.029 and llnl.dat uses 2.2936, but they write it in terms
#                                of HCO3 and consuming a proton.
#  Their HCO3- = CO3-2+H+ log_K is -10.3288, so that equates to -8.0352.  Santos uses -8.29, which looks
#suspiciously like a typo to us.
      delta_h -6.169 kcal

Dypignite
          Mg5(CO3)4(OH)2:5H2O  =  + 5Mg+2  + 4CO3-2 +  2OH- + 5H2O
          log_k                -34.95              #  Santos, 2023; originally from Harrison et al., 2019
          -delta_H 0                    # Not possible to calculate enthalpy of reaction          Dypignite
#         Enthalpy of formation:      0 kcal/mol

Lansfordite
      MgCO3:5H2O + H+  =  + HCO3- + Mg+2 + 5H2O
      log_k          -5.24      # Same for Santos, 2023 & llnl.dat; originally from Hill et al., 1982?
          -delta_H 0


Hydromagnesite
      Mg5(CO3)4(OH)2:4H2O + 6H+  =  + 4HCO3- + 5Mg++ + 6H2O
      log_k          -37.08              # Same for Santos, 2023 & llnl.dat
          -delta_H -289.696kJ/mol   # Calculated enthalpy of reaction Hydromagnesite
#         Enthalpy of formation:      -1557.09 kcal/mol
      -analytic -7.9288e+002 -2.1448e-001 3.6749e+004 3.0888e+002 5.7367e+002
#      -Range:  0-300
Periclase
      MgO + 2H+  =  + 1H2O + 1Mg++
      log_k          21.3354             # llnl.dat
          -delta_H -150.139kJ/mol   # Calculated enthalpy of reaction     Periclase
#         Enthalpy of formation:      -143.8 kcal/mol
      -analytic -8.8465e+001 -1.8390e-002 1.0414e+004 3.2469e+001 1.6253e+002
#      -Range:  0-300
Artinite
      MgCO3:Mg(OH)2:3H2O + 2H+ = 2Mg+2 + CO3-2 + 5H2O
```

```
      log_k          9.3272     #  wateq4f.dat uses 9.6.  llnl.dat uses 19.656, but writes the dissolution as consuming 3
#protons and liberating an HCO3-.
 #     Using the -10.3288 value for converting HCO3- to CO4-2 (see magnesite above), I get 9.3272, which is quite
#close.  Santos et
 #     al., 2023 writes everything in terms of liberating hydroxide instead of consuming protons, so their value is -
#18.67, which
 #     writing it this way, means you add 2X the pKa of water, so -18.67 + 2x14 = 9.33, which is quite close to the # #
llnl.dat value.
 #     So we'll use the llnl as a consensus value.
      -delta_h -28.742 kcal
Brucite
      Mg(OH)2 + 2H+ = Mg+2 + 2H2O
      log_k          16.84  #  llnl.dat uses this, as does Hummel et al. PSI database.  Santos et al., use -11.16 which is
#precisely a difference of 28.00
                #     It looks like Santos et al,. 2023 just wrong this us liberating hydroxide instead of consuming
#protons, so you add 2X the
                #      pKa of water = -11.16 (Santos) + 2*-14 = 16.84 (llnl, Hummel).
      -delta_h -27.1 kcal


END

>>>>>>>>>>>>>>>>>>>>>>>>>>>>>.  XXXXXXXXX.    <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
```

Note: Below are the results file

output file:

```
  Input file: mgo_surf
 Output file: mgo_surf.out
Database file: wateq4f.dat

------------------
Reading data base.
------------------

            SOLUTION_MASTER_SPECIES
            SOLUTION_SPECIES
            PHASES
            EXCHANGE_MASTER_SPECIES
            EXCHANGE_SPECIES
            SURFACE_MASTER_SPECIES
            SURFACE_SPECIES
            RATES
            END
-----------------------------------
Reading input data for simulation 1.
-----------------------------------

            database wateq4f.dat
            SURFACE_MASTER_SPECIES
                  Mgo_s  Mgo_sO
                  Mgo_w  Mgo_wOH2
            SURFACE_SPECIES
                  Mgo_sO = Mgo_sO
```

```
        log_k  0.0
        Mgo_wOH2 = Mgo_wOH2
        log_k  0.0
        Mgo_sO  + H+ = Mgo_sOH+
        log_k  13.5   # = pKa1,int
        Mgo_wOH2 = Mgo_wOH- + H+
        log_k  -5.5   # = pKa2,int
    solution 1
    SURFACE 1
       Mgo_s       2e-5     32.20      4
       Mgo_w       2e-5
    EQUILIBRIUM_PHASES
    PHASES
    Nesquehonite        149
        MgCO3:3H2O = Mg+2 + CO3-2 + 3H2O
        log_k          -5.27    #  Santos, 2023; originally from Harrison et al., 2019
        delta_h -5.789 kcal
    Magnesite
        MgCO3 = Mg+2 + CO3-2
        log_k          -8.029   # Santos, 2023.  wateq4f.dat uses -8.029 and llnl.dat uses 2.2936, but they write it
in terms of HCO3 and consuming a proton.
        delta_h -6.169 kcal
    Dypignite
            Mg5(CO3)4(OH)2:5H2O  =  + 5Mg+2  + 4CO3-2 +  2OH- + 5H2O
            log_k                -34.95                #  Santos, 2023; originally from Harrison et al., 2019
            delta_h   0                    # Not possible to calculate enthalpy of reaction          Dypignite
    Lansfordite
        MgCO3:5H2O + H+  =  + HCO3- + Mg+2 + 5H2O
        log_k          -5.24       # Same for Santos, 2023 & llnl.dat; originally from Hill et al., 1982?
            delta_h   0
    Hydromagnesite
        Mg5(CO3)4(OH)2:4H2O + 6H+  =  + 4HCO3- + 5Mg++ + 6H2O
        log_k          -37.08                # Same for Santos, 2023 & llnl.dat
            delta_h   -289.696kJ/mol    # Calculated enthalpy of reaction Hydromagnesite
        analytical_expression -7.9288e+002 -2.1448e-001 3.6749e+004 3.0888e+002 5.7367e+002
    Periclase
        MgO + 2H+  =  + 1H2O + 1Mg++
        log_k          21.3354              # llnl.dat
            delta_h   -150.139kJ/mol    # Calculated enthalpy of reaction     Periclase
        analytical_expression -8.8465e+001 -1.8390e-002 1.0414e+004 3.2469e+001 1.6253e+002
    Artinite
        MgCO3:Mg(OH)2:3H2O + 2H+ = 2Mg+2 + CO3-2 + 5H2O
        log_k          9.3272     #  wateq4f.dat uses 9.6.  llnl.dat uses 19.656, but writes the dissolution as
consuming 3 protons and liberating an HCO3-.
        delta_h -28.742 kcal
    Brucite
        Mg(OH)2 + 2H+ = Mg+2 + 2H2O
        log_k          16.84  #  llnl.dat uses this, as does Hummel et al. PSI database.  Santos et al., use -11.16
which is precisely a difference of 28.00
        delta_h -27.1 kcal
    END
------------------------------------------
Beginning of initial solution calculations.
------------------------------------------

Initial solution 1.
```

----------Solution composition----------

Elements	Molality	Moles
Pure water		

----------Description of solution----------

pH = 7.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 1.001e-07
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 1.082e-10
Total carbon (mol/kg) = 0.000e+00
Total CO2 (mol/kg) = 0.000e+00
Temperature (deg C) = 25.000
Electrical balance (eq) = -1.082e-10
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.05
Iterations = 0
Total H = 1.110124e+02
Total O = 5.550622e+01

----------Distribution of species----------

Species	Molality	Log Activity	Log Molality	Log Activity	Gamma
OH-	1.002e-07	1.001e-07	-6.999	-6.999	-0.000
H+	1.001e-07	1.000e-07	-7.000	-7.000	-0.000
H2O	5.551e+01	1.000e+00	1.744	0.000	0.000
H(0)	1.416e-25				
H2	7.079e-26	7.079e-26	-25.150	-25.150	0.000
O(0)	0.000e+00				
O2	0.000e+00	0.000e+00	-42.080	-42.080	0.000

----------Saturation indices----------

Phase	SI	log IAP	log KT	
H2(g)	-22.0000	-25.1500	-3.1500	H2
H2O(g)	-1.5100	0.0000	1.5100	H2O
O2(g)	-39.1876	-42.0800	-2.8924	O2

Beginning of batch-reaction calculations.

Reaction step 1.

Using solution 1.
Using surface 1.
Using pure phase assemblage 1.

----------Surface composition----------

Mgo

6.096e-08 Surface charge, eq
4.567e-05 sigma, C/m**2
5.229e-02 psi, V
-2.035e+00 -F*psi/RT
1.307e-01 exp(-F*psi/RT)
3.220e+01 specific area, m**2/g
1.288e+02 m**2 for 4.000e+00 g

Mgo_s

2.000e-05 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mgo_sOH+	2.000e-05	1.000	2.000e-05	-4.699
Mgo_sO	6.534e-11	0.000	6.534e-11	-10.185

Mgo_w

2.000e-05 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mgo_wOH-	1.994e-05	0.997	1.994e-05	-4.700
Mgo_wOH2	6.103e-08	0.003	6.103e-08	-7.214

----------Solution composition----------

Elements	Molality	Moles
Pure water		

----------Description of solution----------

pH = 7.130 Charge balance
pe = -6.356 Adjusted to redox equilibrium
Activity of water = 1.000
Ionic strength = 1.046e-07
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 6.107e-08
Total carbon (mol/kg) = 0.000e+00
Total CO2 (mol/kg) = 0.000e+00
Temperature (deg C) = 25.000
Electrical balance (eq) = -6.107e-08
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -29.18
Iterations = 16
Total H = 1.110124e+02
Total O = 5.550618e+01

----------Distribution of species----------

Species	Molality	Log Activity	Log Molality	Log Activity	Gamma
OH-	1.352e-07	1.351e-07	-6.869	-6.869	-0.000

```
  H+               7.411e-08   7.408e-08    -7.130    -7.130    -0.000
  H2O              5.551e+01   1.000e+00     1.744    -0.000     0.000
H(0)          4.000e-05
  H2               2.000e-05   2.000e-05    -4.699    -4.699     0.000
O(0)          0.000e+00
  O2               0.000e+00   0.000e+00   -82.982   -82.982     0.000

-----------------------------Saturation indices-------------------------------

          Phase               SI log IAP  log KT

          H2(g)           -1.5490   -4.6990   -3.1500  H2
          H2O(g)           -1.5100   -0.0000    1.5100  H2O
          O2(g)           -80.0897  -82.9821   -2.8924  O2

------------------
End of simulation.
------------------
------------------------------------
Reading input data for simulation 2.
------------------------------------
-----------
End of run.
```

xxxxx END OF THE DOCUMENT xxxxx