

## On the thermal decomposition of $\text{MgRh}_2\text{O}_4$ spinel and the solid solution $\text{Mg}(\text{Rh}, \text{Al})_2\text{O}_4$

Christopher J. Capobianco

*Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721 (USA)*

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### Abstract

A precise decomposition curve for stoichiometric  $\text{MgRh}_2\text{O}_4$  was determined experimentally to evaluate its thermodynamic properties. The standard state enthalpy and entropy at 298 K for decomposition to Rh, MgO and  $\text{O}_2$  are  $88.8 \pm 1.9 \text{ kcal mol}^{-1}$  and  $59.8 \pm 1.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ , respectively. A third-law entropy for  $\text{MgRh}_2\text{O}_4$  was estimated for 298 K as  $35.2 \pm 1.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Solid solutions between  $\text{MgRh}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  were prepared that exhibited positive deviations from Vegard's Law. Preliminary data on decomposition of the solid solution are consistent with positive deviations from ideality becoming negative as  $\text{MgAl}_2\text{O}_4$  is approached.

### INTRODUCTION

Recent experimental work has shown that Rh can be strongly concentrated by spinels crystallizing from molten silicate at magmatic temperatures and high oxygen fugacity [1]. But whether a natural magma is able to crystallize spinels with significant Rh, or other platinum-group elements, in solid solution is an unsettled geochemical issue [2]. The problem is the prevailing oxygen fugacities of magma chambers, which seem too low for a non-negligible activity of an oxidized Rh-component. Existing thermochemical data for  $\text{Rh}_2\text{O}_3$  [3] can be used to show that for reasonable magmatic values of temperature, 1200°C, and oxygen fugacity,  $10^{-9}$ , the activity of  $\text{Rh}_2\text{O}_3$  is of the order of  $10^{-15}$  — six orders of magnitude below terrestrial abundances for this element. However this calculation may be misleading, because the solubilities of noble metals in molten silicates are poorly constrained experimentally; in fact, recent work indicates that the dependence on oxygen fugacity may not be as steep as expected from a calculation assuming fully trivalent speciation [4].

However, some spinels crystallize under very high oxygen fugacities, specifically, those formed in molten droplets of silicate ejected into the atmosphere when large meteorites impact the Earth [5]. Spinels produced in these rare impact events can be expected to be anomalously enriched in Rh, but this has not yet been reported, in part due to the difficulty of Rh

analysis. However, iridium, notably the most easily analyzed of the platinum-group elements, has been measured in high abundance in spinel phases associated with sedimentary deposits at the Cretaceous/Tertiary boundary [6, 7] now widely believed to be a result of a large meteorite impact [8]. Recently, high Rh concentrations were reported for Cretaceous/Tertiary boundary sediments [9] using new analytical techniques for Rh.

In the past, synthetic rhodate spinels have been prepared and characterized mostly with respect to crystallographic properties or magnetic properties in ferrite solid solutions [10]. Thermodynamic data pertaining to Rh-bearing spinels are scarce, however. In view of the potential importance of “cosmic” spinels [5] to interpretations of rare but importance occurrences in the geologic record and the lack of fundamental thermodynamic properties pertaining to them, I report here new data on the enthalpy of formation and third-law entropy for  $\text{MgRh}_2\text{O}_4$  spinel. Some preliminary data pertaining to the solid solution of  $\text{MgRh}_2\text{O}_4$  with  $\text{MgAl}_2\text{O}_4$  spinel are also reported.

## EXPERIMENTAL METHODS

### *Synthesis and characterization of $\text{MgRh}_2\text{O}_4$*

Well-crystallized  $\text{MgRh}_2\text{O}_4$  was synthesized from stoichiometric mixtures of  $\text{MgO}$  and  $\text{Rh}_2\text{O}_3$ . The oxides were ground under acetone in an agate mortar and pestle, pressed into wafers, and reacted for several days in a vertical tube furnace at  $1100^\circ\text{C}$  in an atmosphere of pure  $\text{O}_2$ . Unreacted wafers, black because  $\text{Rh}_2\text{O}_3$  is black, become cinnamon-colored during the anneals as  $\text{MgRh}_2\text{O}_4$  is produced. Sharp X-ray powder diffraction peaks were obtained from the run product, all of which were consistent with a spinel-structure phase. The unit-cell parameter of the cubic phase was refined using a least-squares program [11] yielding a value,  $a_0 = 8.501 \pm 0.005 \text{ \AA}$ , consistent with the literature values [12]. Although the sample was too fine-grained for electron microprobe analysis, microscopic examination in grain mounts revealed no unreacted material. Examination with transmission electron microscopy (TEM) revealed well-crystallized material with no microstructure except occasional simple twins (twinned according to the spinel law). All electron diffraction patterns could be indexed on a spinel lattice.

### *Thermal decomposition of $\text{MgRh}_2\text{O}_4$*

The equilibrium investigated is the thermal decomposition of  $\text{MgRh}_2\text{O}_4$ , see reaction (1), where all solid phases are at unit activity. Because there

are three components and four phases, the reaction is univariant and the decomposition equilibrium defines a curve in  $(T, f_{O_2})$  space, where  $f_{O_2}$  is the oxygen fugacity of the system, equal to the partial pressure of oxygen in this case.



To locate the decomposition curve of  $\text{MgRh}_2\text{O}_4$  on a plot of  $P_{O_2}$  versus  $T$ , three gas compositions were chosen with differing but fixed oxygen fugacities. Tightly bracketed points along the decomposition curve were obtained using pure  $\text{O}_2$ , compressed air, and a certified-composition gas mixture containing 7.0%  $\text{O}_2$ , the balance being  $\text{N}_2$ .

The decomposition temperature  $T_D$  was bracketed for each gas mixtures by a series of anneals on small pieces (approximately 3–5 mm<sup>2</sup> and 0.5–1 mm thick) of wafered  $\text{MgRh}_2\text{O}_4$  using a 1.25 in. O.D. vertical tube furnace. The presence or absence of metallic Rh on the run product was used as a criterion for establishing whether the anneal was above or below the equilibrium decomposition temperature.

Alumina crucibles were used to hold the samples which were suspended in a gas-mixing furnace by alumina supports. An alumina-sheathed S-type thermocouple, calibrated against the melting point of Au, measured the run temperature. Initial runs revealed that previous exposure of the muffle tube to Pt causes a shift in  $T_D$  to lower temperatures. In anneals that were made in a Pt-contaminated muffle tube, Rh metal from the run product was analyzed by electron microprobe and found to contain appreciable Pt. Platinum vapor in the muffle tube, resulting from the use of Pt wire sample supports, reduced the activity of metallic Rh in the system and lowered the decomposition temperature.

Overnight anneals typically provided sufficient reaction time to decide whether the run temperature had been above or below the equilibrium reaction boundary. Naturally, closer approaches to the equilibrium decomposition curve took longer to produce Rh crystals. Two- or three-day anneals were used when the decomposition curve was approached closely.

Very precise  $(P_{O_2}, T_D)$  points were determined through microscopic examination of the surface of annealed wafers. Far above  $T_D$  (in the metallic Rh phase field), both top and bottom surfaces of the wafer showed a high surface density of metallic Rh octahedra. Below the reaction boundary, but near to it, the wafer's top surface was free of Rh octahedra, even though the bottom surface sometimes contained metallic Rh crystals. Apparently, the bottom surface was exposed to slightly lower oxygen fugacities, presumably because gas flow was inhibited underneath the sample. Therefore, lower temperature brackets were determined, not by the total absence of Rh crystals, but by their absence on the wafer's top surface. Upper temperature brackets were determined by the presence of Rh crystals on the upper surface. Three  $(P_{O_2}, T_D)$  points were determined;

they were tightly bracketed and therefore required as many as 10–12 separate anneals per point.

An initial attempt to define the equilibrium decomposition curve using thermal gravimetric analysis proved less precise than the static method adopted due to the long time required to decompose the material near to  $T_D$ .

### *Synthesis and characterization of $Mg(Rh_xAl_{1-x})O_4$ solid solutions*

Oxide mixtures of  $MgO$ ,  $Rh_2O_3$  and  $Al_2O_3$  were used as above to prepare solid solutions with  $x = 0.25, 0.5, 0.75$ . Pressed wafers of mixed oxides were annealed in alumina crucibles under pure  $O_2$  for eight days at  $1075^\circ C$ . Two additional compositions at  $x = 0.63$  and  $0.87$  were also reacted for eight days, but at  $1120^\circ C$ . Reaction products ranged in color from reddish-brown to pale yellow depending on Rh content. X-ray powder diffraction patterns on product solid solutions indicated that reaction rates decreased with increasing alumina content. Very sharp diffraction peaks were obtained from pure  $MgRh_2O_4$  but increasingly broadened peaks were produced from samples with increasing amounts of  $Al_2O_3$  in the starting material. However, even in the sample with the broadest peaks, the starting material had completely reacted to form spinel. Apparently, crystallites were formed with a distribution of Rh/Al ratios centred on the bulk composition ratio, producing the broadened diffraction peaks. This was confirmed by TEM examination which revealed well-crystallized individual grains. Further sintering produced little change in powder diffraction patterns because the major chemical driving force, i.e. the free energy of formation for spinel, was dissipated.

Refined lattice parameters for spinel solid solutions were measured and are reported in Table 1. Figure 1 shows these data plotted against mole fraction of  $MgRh_2O_4$ . A positive deviation from Vegard's Law is observed at high concentrations of Rh. Note that deviations from ideal mixing occur for solid solutions which are the most well-crystallized and are therefore least susceptible to error. However, the apparent ideality with respect to lattice parameter for the more Al-rich samples may be simply an artifact

TABLE 1

Spinel lattice parameter  $a_0$  in Å for  $Mg(Rh_xAl_{1-x})O_4$  solid solutions (standard error for least significant digit of  $a_0$  given in parentheses)

$x$	0.0	0.25	0.5	0.63	0.75	0.87	1.0
$a_0$	8.0855(6) <sup>a</sup>	8.185(5)	8.308(7)	8.368(6)	8.436(3)	8.472(4)	8.502(7)

<sup>a</sup> Ref. 13.

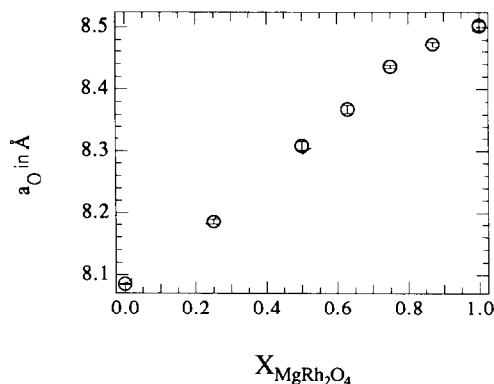


Fig. 1. Spinel unit cell parameter  $a_0$  in Å versus mole fraction of  $\text{MgRh}_2\text{O}_4$  in solid solution with  $\text{MgAl}_2\text{O}_4$  ( $\pm 1$  standard error shown inside symbols).

arising from the distribution of crystal compositions within the powdered sample which are centered on the bulk composition.

#### *Thermal decomposition of $\text{Mg}(\text{Rh}_x\text{Al}_{1-x})\text{O}_4$ solid solutions*

Preliminary experiments investigating reaction (1) for a four-component system were attempted. The fourth component,  $\text{MgAl}_2\text{O}_4$ , dilutes the  $\text{MgRh}_2\text{O}_4$  activity in spinel solid solution and reduces the oxygen fugacity required to maintain equilibrium. At fixed temperature and pressure, spinel compositional dependence on oxygen fugacity provides information on the mixing properties of the solid solution. The appropriate equilibrium constant, based on reaction (1), is

$$\ln K_{\text{EQ}} = 3/2 \ln f_{\text{O}_2} - \ln a_{\text{MgRh}_2\text{O}_4}^{\text{spinel}} \quad (2)$$

Two isothermal (1139°C) solid solution decomposition runs were made. Despite the disadvantage that they are difficult to prepare in well-crystallized form, Al-rich spinels were used because they better constrain non-ideal activity for the Rh component, which must tend toward Raoultian behavior when the spinel is Rh-rich.

Samples held in alumina crucibles were annealed under flowing  $\text{O}_2/\text{N}_2$  gas mixtures with well-defined oxygen fugacities. The first run, at an oxygen fugacity of 0.6, annealed for eight days wafers of composition: (1) spinel with  $x = 0.63$ ; (2) mixture of spinel with  $x = 0.5$  and excess  $\text{MgO}$  and  $\text{Rh}_2\text{O}_3$  to give a bulk composition of  $x = 0.65$ ; (3) unreacted oxides with bulk composition of  $x = 0.5$ . The second run, at the oxygen fugacity of air, 0.209, annealed for 31 days samples with  $x = 0.17$ , 0.25 and 0.33. Pure Rh-spinel was added to the 0.17 and 0.25 samples. At equilibrium only a single-composition spinel should be found in each crucible coexisting with  $\text{MgO}$  and Rh.

## RESULTS AND DISCUSSION

*MgRh<sub>2</sub>O<sub>4</sub>*

Table 2 gives the equilibrium decomposition temperature  $T_D$  for the three oxygen fugacities  $f_{O_2}$  investigated. The enthalpy and entropy for the decomposition reaction is calculated from the temperature dependence of the equilibrium constant of reaction (1)

$$R \ln K_{EQ} = 1.5R \ln f_{O_2} = -\frac{\Delta H_T^\ominus}{T} + \Delta S_T^\ominus \quad (3)$$

Enthalpy and entropy terms calculated from regressions of experimental ( $f_{O_2}$ ,  $T_D$ ) points pertain to the range of experimental temperature  $990 < T < 1140$ . The values obtained are reported in Table 3 along with  $1\sigma$  errors obtained by a Monte Carlo error analysis technique [14]. Only small uncertainties arise because the temperature dependence described in eqn. (3) is a good approximation over the temperature interval investigated. This implies that effects from a finite  $\Delta C_p$  of reaction (1) can be ignored in this temperature interval.

To calculate thermodynamic parameters for the 298 K standard state from high temperature data, heat capacity effects cannot be ignored. The general equation, eqn. (4), can be used to extract the 298 K values from high temperature experimental data

$$\Delta G_T^\ominus = \Delta H_{298}^\ominus + \int_{298}^T \Delta C_p \, dT - T \left( \Delta S_{298}^\ominus + \int_{298}^T \frac{\Delta C_p}{T} \, dT \right) \quad (4)$$

Heat capacities are available for all phases except  $MgRh_2O_4$  which must be

TABLE 2

Decomposition of  $MgRh_2O_4$  spinel at 1 atm

$f_{O_2}$	$T_D$
1.0	$1139 \pm 1.5^a$
0.0209	$1045 \pm 2.0$
0.070	$991 \pm 1.0$

<sup>a</sup>  $T_D$  in °C is estimated as the midpoint of the interval defined by the upper and lower temperature brackets, the error is half the interval.

TABLE 3

Thermodynamic parameters derived from the decomposition of  $MgRh_2O_4$  (in calorie units)

$\Delta H_{298}^\ominus$	$\Delta S_{298}^\ominus$	$S_{MgRh_2O_4, 298}^\ominus$	$\Delta H_T^\ominus$	$\Delta S_T^\ominus$
$88800 \pm 1900$	$59.8 \pm 1.4$	$35.2 \pm 1.5$	$95200 \pm 700^a$	$67.5 \pm 0.5^a$

<sup>a</sup> Values pertain to an average temperature,  $990 < T < 1140^\circ\text{C}$ .

approximated. The approximation of eqn. (5) [15] that the stoichiometric sum of the heat capacities of constituent oxides is equal to the heat capacity of the compound oxide is used, where  $\nu_i$ , indicates the number of moles of oxide  $i$  in the compound

$$C_p(\text{compound oxide}) = \sum_i \nu_i C_p(\text{simple oxide})_i \quad (5)$$

In this approximation  $\Delta C_p$  for reaction (1) becomes the  $\Delta C_p$  for the decomposition of  $\text{Rh}_2\text{O}_3$ , which is available from the literature [3].

The simplified expression used in the least-squares regression of high-temperature experimental data is given in eqn. (6) where  $h(T)$  and  $s(T)$  are evaluated from the heat capacity integrals in eqn. (4) at  $T_D$

$$1.5R \ln f_{\text{O}_2} - h(T) - s(T) = -\frac{\Delta H_{298}^\ominus}{T} + \Delta S_{298}^\ominus \quad (6)$$

The left-hand side of eqn. (6) is completely specified by  $(f_{\text{O}_2}, T_D)$  pairs. Figure 2 plots the left-hand side of this equation against reciprocal temperature. The 298 K thermodynamic parameters are given in Table 3 along with  $1\sigma$  Monte Carlo errors which include uncertainties associated only with  $T_D$  determinations.

The third-law entropy for  $\text{MgRh}_2\text{O}_4$  may be calculated from the 298 K entropy of reaction (1) determined here using the equation

$$S_{\text{MgRh}_2\text{O}_4,298}^\ominus = S_{\text{MgO},298}^\ominus + 3/2S_{\text{O}_2,298}^\ominus + 2S_{\text{Rh},298}^\ominus - \Delta S_{298}^\ominus \quad (7)$$

Values for the standard entropies of the products of reaction (1) were taken from the literature [3]. The entropy for  $\text{MgRh}_2\text{O}_4$  spinel is determined as  $35.2 \pm 1.5 \text{ cal mol}^{-1} \text{ K}^{-1}$  with a  $1\sigma$  error arising from the uncertainty in the experimentally determined entropy of decomposition.

If one uses the literature value of  $22 \pm 3.5 \text{ cal mol}^{-1} \text{ K}^{-1}$  for the entropy of  $\beta\text{-Rh}_2\text{O}_3$  [3], the entropy for  $\text{MgRh}_2\text{O}_4$  spinel is nearly 20% larger than

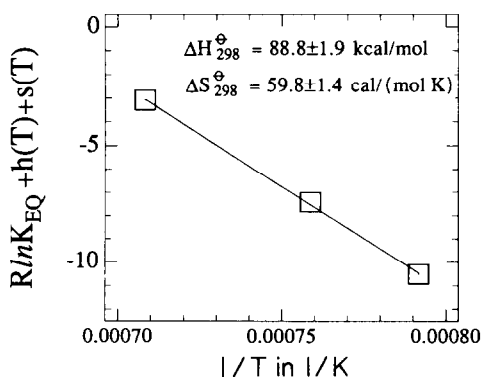
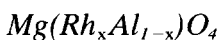


Fig. 2. Extraction of 298 K thermodynamic parameters for reaction (1), see eqn. (6).

the sum of the entropies of MgO and Rh<sub>2</sub>O<sub>3</sub>. Due to the high octahedral-site preference of Rh<sup>3+</sup> [10], it is unlikely that the high entropy of the Rh spinel is associated with cation disorder in the spinel. All known rhodate spinels are *normal* spinels with all Rh in octahedral sites. There are no cryogenic heat capacity data available for β-Rh<sub>2</sub>O<sub>3</sub>; thus all estimates of its 298 K third-law entropies are based on chemical reaction thermodynamics [12]. Higher estimates of the entropy of β-Rh<sub>2</sub>O<sub>3</sub> exist, e.g., 26.5 cal mol<sup>-1</sup> K<sup>-1</sup> [12], which would yield a spinel entropy more consistent with expectations of the additivity of oxide entropies; however, consideration of the energetics of spinel formation from the oxides suggests that a large entropy of formation from the oxides is reasonable.

The enthalpy of dissociation of MgRh<sub>2</sub>O<sub>4</sub> spinel at 298 K, 88.8 kcal mol<sup>-1</sup>, is slightly less endothermic than the enthalpy of dissociation for Rh<sub>2</sub>O<sub>3</sub>, 91.5 ± 4.0 kcal mol<sup>-1</sup> [3]. The similarity of these values implies that formation of Rh spinel from the oxides is not energetically favored at 298 K, with an endothermic heat of formation from the oxides of 2.7 ± 4.4 kcal mol<sup>-1</sup>. For comparison, MgAl<sub>2</sub>O<sub>4</sub> is favored by -10.6 kcal mol<sup>-1</sup> with respect to its oxide components at 298 K [16]. However, MgRh<sub>2</sub>O<sub>4</sub> spinel forms easily from the oxides at elevated temperatures, suggesting significantly enhanced stability with increasing temperature—a consequence of its positive entropy of formation from the oxides.



The temperature chosen for the solid solution decomposition is the experimentally determined  $T_D$  for pure MgRh<sub>2</sub>O<sub>4</sub> at  $f_{O_2} = 1$ . Thus, the left-hand side of eqn. (2) equals zero and the activity of the Rh component of the spinel is simply related to the equilibrium oxygen fugacity

$$(f_{O_2})^{3/2} = a_{MgRh_2O_4}^{spinel} \quad (8)$$

Because there are two moles of cations mixing per formula unit, the activity is related to the mole fraction [17]

$$a_{MgRh_2O_4}^{spinel} = \gamma_{MgRh_2O_4}^{spinel} (x_{MgRh_2O_4}^{spinel})^2 \quad (9)$$

This formulation presumes mixing of Al and Rh only on the octahedral sites of spinel. A simple activity–composition relationship is used to examine the new results. A simple regular solution model is sufficient, where

$$\ln \gamma_{MgRh_2O_4}^{spinel} = \frac{\Omega}{RT} (1 - x_{MgRh_2O_4}^{spinel})^2 \quad (10)$$

The eight-day decomposition run at  $f_{O_2} = 0.6$  did not produce an equilibrium assemblage in any of the charges. Nevertheless, some thermodynamic information was obtained. The surface of the  $x = 0.63$  anneal was



covered with Rh crystals, even though the interior was barren. The anneal was not long enough to decompose the bulk sample and enable a measurement of the equilibrium spinel composition. However, a lower limit to  $\Omega$  can be fixed at  $3200 \text{ cal mol}^{-1}$  using  $x = 0.63$ . A positive deviation from ideality is consistent with non-ideal behavior found in the lattice parameters. The volume mismatch [18] between Al and Rh is also consistent with positive deviations from ideal mixing.

The second run, 31 days at  $f_{\text{O}_2} = 0.209$ , was also insufficient to produce homogeneous spinel phases in any of the three charges. Run products still provided some constraints on the mixing behavior. The  $x = 0.33$  sample remained undecomposed, setting an upper limit to  $\Omega$  at  $-800 \text{ cal mol}^{-1}$  and indicating a significant compositional dependence to  $\Omega$ . The sample containing a mixture of  $x = 0.17$  and pure  $\text{MgRh}_2\text{O}_4$  produced an X-ray diffraction pattern with Rh metal peaks and doubled spinel peaks. A composition of approximately  $x = 0.54$  was indicated by the  $d$  spacings of peaks of the Rh-rich spinel, suggesting that significant reaction had occurred. With this spinel compositional estimate, a lower limit for  $\Omega$  can be set at  $-15000 \text{ cal mol}^{-1}$ . Thus, the data from the two decomposition runs indicate that  $\Omega$  must vary with composition.

Data more precise than these are required to quantify the compositional dependence of  $\Omega$ , but the simple regular solution model, eqn. (10), seems inadequate. Pure  $\text{MgAl}_2\text{O}_4$  is partially disordered at  $1139^\circ\text{C}$  [13, 19], with some mixing of Mg and Al between tetrahedral and octahedral sites. This may help explain the decrease in positive deviations from ideality for Al-rich compositions. Strain energy associated with cation size mismatch between Al ( $0.53 \text{ \AA}$ ) and Rh ( $0.68 \text{ \AA}$ ) on octahedral sites would be lessened when Mg ( $0.715 \text{ \AA}$ ) replaces Al on octahedral sites (radii from ref. 20).

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