

IMPACT INDUCED DEHYDRATION OF SERPENTINE AND THE
EVOLUTION OF PLANETARY ATMOSPHERES

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Abstract. Shock recovery experiments in the 25 to 45 GPa range on antigorite serpentine determine the amount of shock-induced loss of structural water as a function of shock pressure. Infrared absorption spectra of shock recovered samples demonstrate systematic changes in the amount of structural water and molecular, surface adsorbed water. These yield qualitative estimates of shock-induced water loss and demonstrate that a portion of the shock released structural water is reabsorbed on interfacial grain surfaces. Determination of the post-shock water content of the shocked samples relates shock-induced water loss and shock pressure. Based on the present results and theoretical predictions, we conclude that shock pressures of from 20 to ~60 GPa induce incipient to complete water loss, respectively. This result agrees closely with theoretical estimates for total dehydration. The dehydration interval and the activation energies for dehydration in shocked samples decrease systematically with increasing shock pressure as experienced by the sample. We believe the present experiments are applicable to describing dehydration processes of serpentine-like minerals in the accretional environment of the terrestrial planets. We conclude that complete loss of structural water in serpentine could have occurred from accretional impacts of ~3 km/sec when earth and Venus have grown to about 50% of their final size. Accreting planetesimals, impacting Mars, never reached velocities sufficient for complete dehydration of serpentine. Our results support a model in which an impact generated atmosphere/hydrosphere forms while the earth is accreting.

Introduction

We report results of shock recovery experiments carried out on antigorite serpentine ($Mg_3Si_2O_5(OH)_4$). The main objective of this study is the determination of critical shock pressures for partial and complete dehydration of serpentine under shock loading.

Serpentine and serpentine-like layer silicates are the major water-bearing phases in carbonaceous chondrites [Wilkening, 1978, Barber, 1981]. It appears that these minerals, and a poorly defined cometary contribution, were the most likely water-bearing phases in accreting planetesimals which led to the formation of the terrestrial planets. In models proposed by Arrhenius et al. [1974], Benlow and Meadows [1977], and Lange and Ahrens [1980, 1982a] formation of a planetary atmosphere/hydrosphere is envisioned as a primary process, taking place during accretion. Water and other volatiles in minerals of the infalling

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planetesimals are released when these bodies hit the accreting planets, and is continually added to a growing proto-atmosphere. Arrhenius et al. [1974] propose, based mainly on noble gas abundance patterns in the present terrestrial atmosphere, that the earth's atmosphere and hydrosphere are primarily the result of such an initial process and have since undergone only minor alteration. In our earlier models [Lange and Ahrens 1980, 1982a] we demonstrated that the effects of a major sink for atmospheric water, the hydration of nonhydrous surface minerals (mainly pyroxene and olivine) would be negated by repeated dehydration of surface layers due to impacting planetesimals. Based on a model for the accretion rate of the terrestrial planets and the volatile content of the planetesimals, critical parameters for the generation of a primary atmosphere were determined, parameters which have likely been met by the accretional environment on earth [Lange and Ahrens, 1982a].

Important parameters for these models are the physical conditions leading to the dehydration of hydrous minerals under shock loading (more generally, to the devolatilization of volatile-bearing minerals), e.g., the critical impact pressure P_{cr} for partial or complete water loss [Lange and Ahrens, 1980, 1982a]. The value for complete dehydration ($P_{cr} = 60$ GPa) was determined theoretically [Lange and Ahrens, 1979] using the entropy gain method of Ahrens and O'Keefe [1972]. However, as P_{cr} is critically dependent on the Grüneisen parameter of serpentine, which is only poorly constrained, the theoretical value may be somewhat in error.

Boslough et al. [1980] first demonstrated the loss of structural water in shocked antigorite serpentine in vapor recovery experiments. In the present experiments, shock-induced water loss in antigorite serpentine was quantitatively determined from comparison of the amount of post-shock water in recovered samples with that initially present [Lange and Ahrens, 1982b]. Qualitative estimates for loss of structural water were also obtained from infrared spectra of shocked and unshocked samples.

Experimental Details

The material used in the experiments is antigorite serpentine ($Mg_3Si_2O_5(OH)_4$) from Thurman, New York, with an initial density of 2.54 ± 0.004 g/cm³. The major oxide composition of the material determined from a 10 point microprobe analysis is given in Table 1. As can be seen, the measured composition is close to the theoretical value. The initial amount of structural water in the samples (12.6 wt. %) was determined by use of a Mettler Thermoanalyzer TA 2000C on an unshocked reference sample.

Sample discs, 4.4 mm in diameter, 0.5 mm thick, were polished flat and parallel to within ± 2

Table 1. Composition of sample material, Antigorite Serpentine, Thurman, New York

	MgO	SiO ₂	Na ₂ O	Al ₂ O ₃	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	H ₂ O ⁺	others [†]
Mean value*, wt. %	41.007	42.726	0.011	0.196	0.028	0.022	0.007	0.023	0.485	12.6	2.895
Standard deviation*, wt. %	0.190	0.383	0.014	0.057	0.005	0.014	0.012	0.032	0.113	0.2	-
Theoretical value, wt. %	43.64	43.36								13.0	

* Based on 10 point microprobe analysis, A. Chodos, analyst.

+ Measured with thermogravimetric analyzer, Mettler TA 2000C.

† Inferred.

microns and were inserted into stainless steel sample assemblies which are schematically shown in Figure 1. The assemblies are of a design which allow the escape of released volatiles (vented assemblies) (Figure 1b). Dehydration of hydrous minerals depends critically on the ambient partial pressure of water vapor [Brindley et al., 1967]. As a consequence, in earlier experiments on brucite, in sample configurations which did not allow the escape of released water vapor (sealed assemblies), shock-induced dehydration of the samples was limited and could not systematically be related to the shock pressures reached in these experiments [Lange, unpublished data].

Stainless steel or aluminum flyer plates were accelerated in a 20 mm powder gun and impacted the recovery assemblies with velocities between ~1.4 to 1.9 km/s inducing peak shock pressures of 25 to 45 GPa in the sample discs (Table 2). Upon recovery, the sample discs were in most cases mechanically intact. Their color had changed from a greenish yellow to a grayish or greenish white. The almost translucent samples became opaque upon shock loading, probably due to extensive formation of microcracks.

Infrared spectra of the unshocked and shocked sample material were obtained by employing the techniques described by Boslough et al. [1980]. For most of the experiments, 5 mg of the shocked sample was used for analysis in a Mettler Thermoanalyzer 2000 C, to determine the amount of structural water retained in the shocked samples. By comparison of this value with initially present water, a quantitative determination of shock-induced water loss was obtained (Table 2).

Experimental Results and Discussion

Infrared Spectroscopy

Infrared absorption spectra for unshocked and a series of shocked antigorite samples are shown in Figure 2. Prominent absorption peaks, corresponding to the presence of structural water (=a, at 3690 cm⁻¹), molecular, i.e., surface adsorbed water (= b and c, at 3450 cm⁻¹ and 1630 cm⁻¹, respectively), and Si-O bond vibrational modes (=d and e, at 950 cm⁻¹ and 445 cm⁻¹, respectively) are indicated [Farmer, 1974]. An obvious result of increasing shock pressure is the reduction in the structural water absorption peak, in good agreement with observations of Boslough et al. [1980] for antigorite serpentine and nontronite. To quantify changes in peak heights, we plotted these heights, relative to each other as a function of shock pressure (Figure 3). The structural water peak (= a) decreases significantly, both with respect to the peaks representing surface adsorbed water as well as with respect to the Si-O bond vibrational mode absorption, indicating qualitatively a decrease in structural water with increasing shock pressure. The increase in the peak heights corresponding to molecular, surface adsorbed water (b and c), suggests that fractions of the structural water released upon shock loading become adsorbed and remain in the sample material. This surface adsorbed water was removed by evacuating the

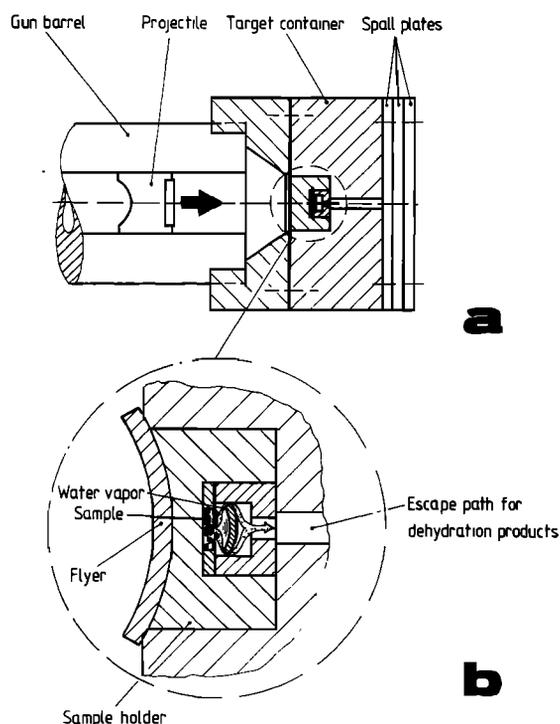


Fig. 1. Schematic configuration of target assembly used in present recovery experiments: (a) depicting the configuration immediately before projectile impact, (b) shows some of the details during shock loading. Escape of dehydration products (water vapor) is provided by the passage of vapor around the moving (away from the shock front) plate which is initially in contact with shock loaded sample.

Table 2. Shock loading condition for serpentine and water loss

	Shot No.			
	683	685	687	690
Sample Mass, g	0.0194	0.0193	0.0194	0.0191
Impactor	Aluminum	Stainless Steel	Stainless Steel	Stainless Steel
Velocity, km/s	1.90	1.28	1.55	1.89
Peak pressure, GPa	25.0	31.8	36.0	45.0
Post shock water content, wt. %	9.02	7.20	4.97	2.99
Shock induced water loss, wt. %	28.4	42.9	60.6	76.3

sample chamber ($\leq 10^{-2}$ mm Hg) in the thermogravimetric analysis of the shocked samples. This is comparable to the findings of Boslough et al. [1980] in that the only peaks sensitive to sample preparation and handling were those corresponding to molecular water. They found that the height of the absorption peaks, which showed the same increase with increasing shock pressure as observed here, were significantly reduced after heating the sample material for several hours at 100°C under vacuum.

Thermogravimetric Analysis

Mass loss curves of unshocked and shocked antigorite serpentine are given in Figure 4. Mass

loss given in weight percent relative to the sample mass (in most cases 5 mg), occurs in the 800–900K region, with a mean of 856.4 ± 10.5 K. From the close correspondence with dehydration temperatures reported by other investigators [=873K, Brindley et al., 1967], we infer that the mass decrease represents loss of structural water. As vaporization temperatures for other major

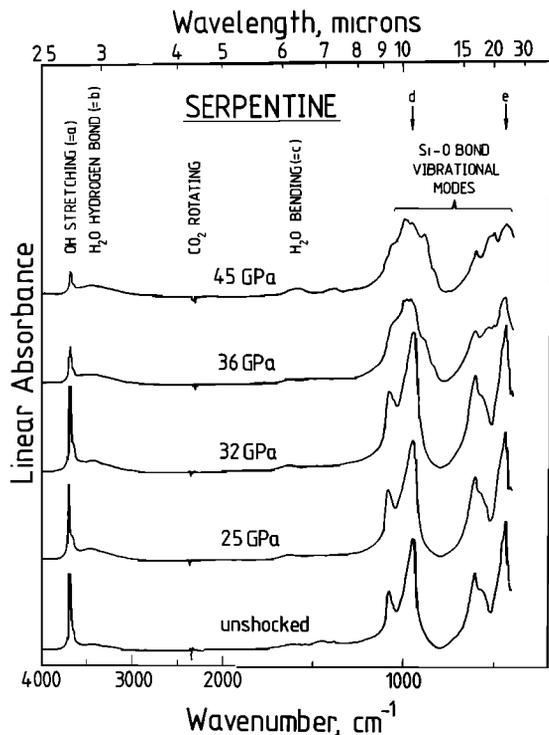


Fig. 2. Infrared absorption spectra of unshocked and shocked antigorite serpentine; the shock pressure is indicated for each spectrum.

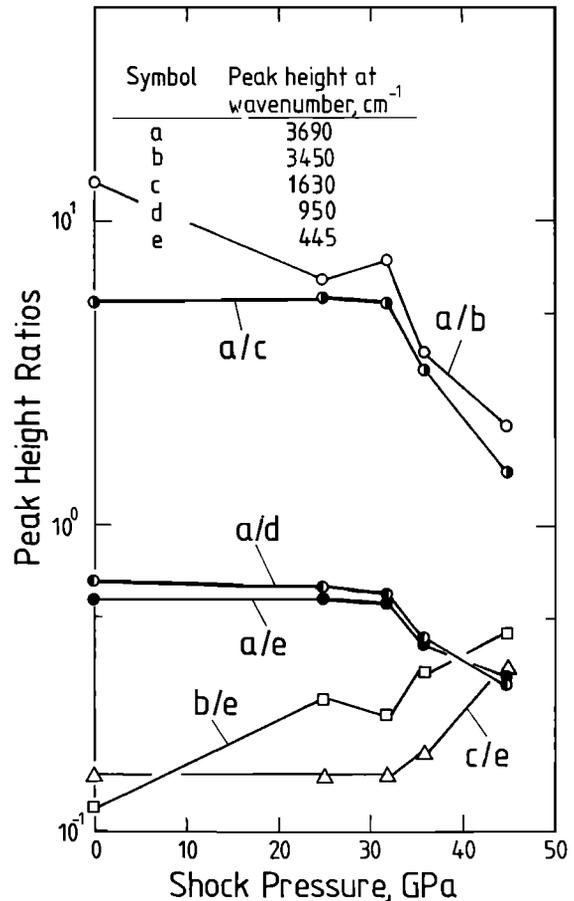


Fig. 3. Ratios in peak heights of absorption spectra of antigorite serpentine as a function of shock pressure. Symbols are the same as those indicated in Figure 2.

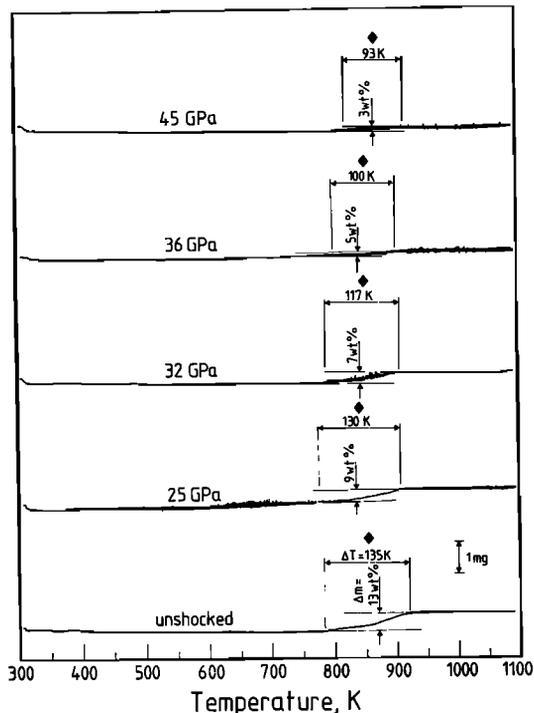


Fig. 4. Mass loss curves for unshocked and shocked antigorite serpentine as a function of temperature. Mass loss corresponds to loss of structural water in the shocked samples. For each curve, the length of the dehydration interval and the post-shock water, relative to the sample mass are indicated. The dehydration temperature, taken as the median of the dehydration interval, is indicated by a solid diamond.

phases present in the samples (MgO, SiO₂) lie at substantially higher temperatures than those reached in our analysis, these reactions will not contribute to the mass loss. The absence of detectable mass loss at temperatures <373K, which would denote the loss of surface adsorbed water, indicates that the evacuation of the sample chamber removed most of the molecular water prior to the analysis.

The dehydration interval (i.e., the temperature interval over which dehydration of a sample occurs) becomes narrower with increasing shock pressure (Figure 4), although no systematic change in the dehydration temperature (taken as the median of the dehydration interval) was observed (Table 3). The progressively smaller amounts of structural water released in the thermogravimetric analysis reflect an increasingly greater amount of shock-induced dehydration with increasing shock pressure. Taking the water loss of the unshocked samples (i.e., 12.6 wt. %) as representing 100% of the total structural water, the mass loss of a shocked sample, representing water retained through the shock event, can be used to calculate the shock-induced water loss (Figure 5). The empirical relationship between shock-induced water loss, WL (wt. %), and shock pressure, P(GPa), for antigorite serpentine is represented by the curve in Figure 5 and is given by:

$$WL = -63.7 + 4.3P - 0.03P^2 \quad (1)$$

Extrapolation of these data, indicates that dehydration of serpentine occurs at shock pressures between ~20 GPa (incipient dehydration) and ~60 GPa (complete dehydration). Data of Boslough et al. [1980] for one successful vapor recovery experiment on antigorite serpentine are also given in Figure 5. It is in good agreement with the trend defined in (1) may indicate an insufficient recovery rate of water vapor, and demonstrates the difficulties of vapor recovery experiments. Also indicated in Figure 5 is the theoretical point for complete water loss [Lange and Ahrens, 1979, 1980]. The good agreement of the extrapolated curve with the theoretical value indicates the validity of the entropy gain method used by Ahrens and O'Keefe [1972] to predict the onset of shock-induced dehydration, and establishes the validity of material parameters used in the calculations of Lange and Ahrens [1980]. In applying the entropy gain method, it is assumed that in exceeding the critical entropy for complete dehydration during shock loading, isentropic decompression of the shocked sample leads to the removal of structural water from individual crystals during the decompression phase [Lange and Ahrens, 1982a]. This process is schematically depicted in Figure 1b.

The systematic decrease in the dehydration interval with increasing pressure indicates a decrease in the activation energies (energy of association) [Nutting, 1943] required for dehydration in the thermogravimetric analysis. In order to quantify this effect we computed, based on the mass loss curves of Figure 4, the sample mass M relative to the weight of the dehydrated sample, i.e., the sample mass at 1000K:

$$M = m(T)/m(1000) \quad (2)$$

where m is the sample mass at a particular temperature. M reaches 1 upon completion of the dehydration reaction. A plot of log₁₀ M versus 10³/T for hydrous minerals results, in most cases,

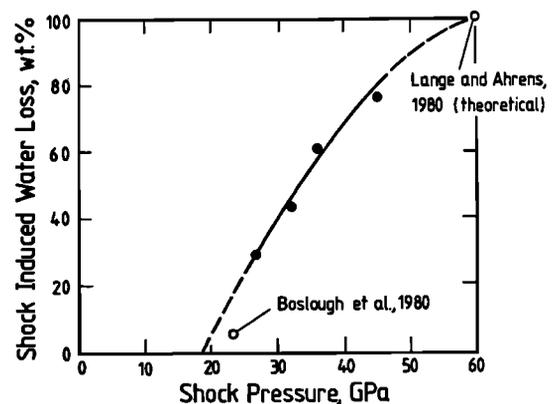


Fig. 5. Shock-induced water loss (in wt. % of the total amount of structural water in antigorite) in antigorite serpentine as a function of shock pressure as inferred from the amount of measured post-shock water. Points from a vapor recovery experiment of Boslough et al. [1980] and a theoretical prediction for complete water loss in serpentine [Lange and Ahrens, 1979, 1980] are indicated.

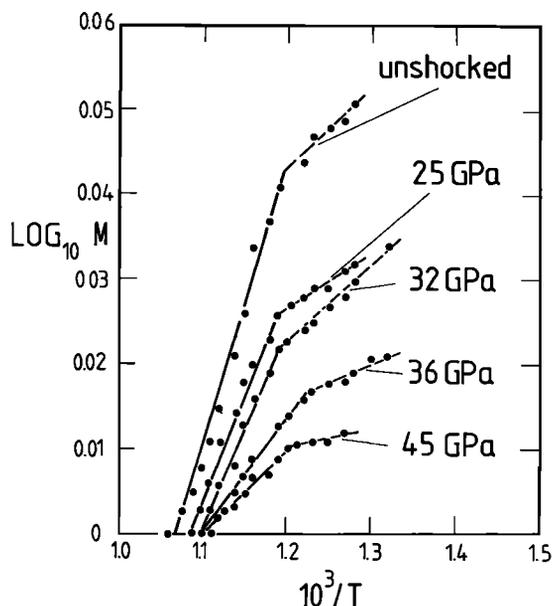


Fig. 6. Relative sample weights M ($= m(T)/m(1000K)$, m = sample mass as a function of temperature) as a function of reciprocal temperature for unshocked and shocked antigorite serpentine. Slopes of the solid straight lines are a measure of the activation energy in dehydration reaction and decrease with increasing shock pressure.

in a linear relationship comprising three segments (Figure 6, the third segment coincides with the x-axis of the plot). The slope of the segment corresponding to the dehydration interval is a measure of the activation energy of the dehydration reaction [Nutting, 1943], and values derived are given in Table 3. Activation energies for the release of post-shock water show a systematic decrease with increasing shock pressure. This implies that changes in the crystal structures of these minerals, in particular a weakening of bonds between OH^- -groups and other constituents of the crystal lattice, correspond to the degree of shock loading.

Conclusions and Implications

The systematic variation in the peak heights of infrared absorption spectra for shocked antigorite serpentine provides a useful tool for the qualitative estimate of shock-induced alteration in hydrous minerals. An increase in molecular water in the shocked samples, indicated by increasing peak heights for H_2O hydrogen bonding and H_2O bonding modes, suggests that some of the structural water, released upon shock loading is adsorbed at grain interfaces. A quantitative relation between the amount of shock-induced water loss and shock pressure (equation (1)) is derived from thermogravimetric analysis of the shock loaded samples. Incipient to complete dehydration of serpentine requires shock pressures in the range from ~ 20 GPa to 60 GPa, respectively. The close agreement between the present experimental results and theoretical estimates for complete dehydration [Lange and Ahrens, 1980] indicates that the entropy gain method to quantify

shock-induced dehydration [Ahrens and O'Keefe, 1972] is applicable. The removal of post-shock water in the present samples, by thermogravimetric analysis, takes place over decreasing temperature intervals with increasing shock pressure. This effect is quantitatively demonstrated as the activation energies of dehydration, which show a parallel decrease with increasing shock pressure. We interpret this as a weakening of hydroxyl bonds in the shocked lattices.

The data presented can be applied to models of an impact generated atmosphere [Lange and Ahrens, 1980, 1982a]. If we assume that impact velocities of infalling planetesimals are close to the escape velocity on the accreting terrestrial planets [Lange and Ahrens, 1982a], these velocities will increase as a function of the enlarging radius, r , and increasing mass, m , of the planet. Major, nonferric minerals comprising most of the terrestrial planets are forsterite, enstatite, and anorthite. They have shock impedances ($= \rho C_0$, ρ = zero pressure density, C_0 = bulk sound speed) between 8.3 and 9.3×10^5 g/sec cm^2 , which are slightly above the value for serpentine ($= 7.7 \times 10^5$ g/sec cm^2) [Lange and Ahrens, 1982a]. For materials with similar shock impedances, impact velocities required to induce a certain shock pressure in impactor and target material, are equal to twice the particle velocity at this pressure. Particle velocities induced in the shocked minerals can be related to shock pressures using equation of state data for serpentine [Marsh, 1980]. Hence we can replace the pressure axis in Figure 5 by an axis giving twice the particle velocity in shocked serpentine. By equating these velocities with the escape velocity of a growing planet, we can plot the amount of shock-induced water loss in serpentine as a function of radius or (by using appropriate mean densities) mass of an accreting planet. In Figure 7, relative radius (r/R , R = final planetary radius) and relative mass (m/M , M = final planetary mass) are plotted versus the amount of shock-induced water loss. We thus can specify the stages in the accretional sequence of the larger, and hence more volatile-rich, terrestrial planets

Table 3. Dehydration of unshocked and shocked samples

	unshocked	Shot No.			
		683	685	687	690
Shock pressure, GPa	-	25.0	31.8	36.0	45.0
Dehydration temperature, K	856	844	853	856	873
Dehydration interval, deg	135	130	117	100	93
Activation energy, kcal/mol	1.56	1.17	1.10	0.64	0.43

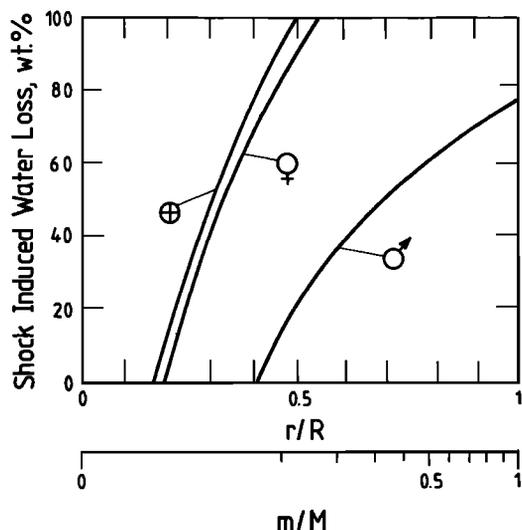


Fig. 7. Shock-induced water loss in antigorite (in wt. % of the total amount of structural water in antigorite) as a function of relative size (r/R) and relative mass (m/M) of the accreting terrestrial planets. Dehydration of antigorite in infalling planetesimals and proto-crusts of growing planets takes place when the threshold pressures as given in Figure 5 are exceeded. This takes place at different stages in the accretional sequence for each planet, the position of which depends on the mean density and the final size of the planetary body as given by the curves for earth (\oplus), Venus (\ominus), and Mars (\circ). Further details, see text.

corresponding to various degrees of water loss from the hydrous minerals in accreting planetesimals and their resulting proto-crusts. This provides a boundary condition for models of an impact generated atmosphere [Lange and Ahrens, 1982a]. As can be seen in Figure 7, incipient, shock-induced dehydration of serpentine minerals is initiated when earth and Venus have reached about 20% of their final size, while this stage is reached for Mars not before it has grown to ~45% of its final radius. Fifty percent dehydration takes place for $r/R \approx 0.32$ for earth and Venus and $r/R \approx 0.7$ for Mars. Rapid growth of an impact generated atmosphere/hydrosphere starts when complete dehydration of serpentine-like minerals in planetesimals and proto-crusts of the accreting planets is initiated. Mars never reaches this stage and earth and Venus have to grow to ~50% of their final size. At this point, infalling planetesimals hit the accreting earth and Venus with velocities of ~3 km/s.

The process of impact induced devolatilization of volatile bearing minerals during accretion represents only one major process in the evolution of a primary planetary atmosphere [Lange and Ahrens, 1982a]. The present results imply that such a process is likely to have occurred on earth and lends support to the model of a terrestrial atmosphere/hydrosphere forming during the later stages of accretion of the earth.

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