Metastable Phases in Polar Stratospheric Aerosols

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Phase changes in stratospheric aerosols were studied by cooling a droplet of sulfuric acid (H_2SO_4) in the presence of nitric acid (HNO_3) and water vapor. A sequence of solid phases was observed to form that followed Ostwald's rule for phase nucleation. For stratospheric partial pressures at temperatures between 193 and 195 kelvin, a metastable ternary H_2SO_4 -HNO_3 hydrate, $H_2SO_4 \cdot HNO_3 \cdot 5H_2O$, formed in coexistence with binary $H_2SO_4 \cdot kH_2O$ hydrates (k = 2, 3, and 4) and then transformed to nitric acid dihydrate, HNO_3 $\cdot 2H_2O$, within a few hours. Metastable HNO_3 $\cdot 2H_2O$ always formed before stable nitric acid trihydrate, HNO_3 $\cdot 3H_2O$, under stratospheric conditions and persisted for long periods. The formation of metastable phases provides a mechanism for differential particle growth and sedimentation of HNO_3 from the polar winter stratosphere.

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m vpe}$ I polar stratospheric clouds (PSCs) form during winter at temperatures between 192 and 195 K, which is 2 to 4 K above the frost point for water ice (1-3). PSCs provide surfaces for hydrolysis of ClNO₃ (4) and for oxidation of HCl (5) to produce high concentrations of chlorine radicals [ClO and $(ClO)_2$] (6, 7). If a large amount of HNO₃ remains in the spring, the chlorine radicals are removed by reaction with NO and NO₂ derived from HNO₃ photolysis. Nearly complete loss of O_3 (through ClO-catalyzed destruction) is observed only where HNO₃ is removed from the atmosphere; hence, differential growth and sedimentation of PSC particles regulate polar O₃ loss (2–5, 8, 9).

Models for PSC formation usually assume nucleation of nitric acid trihydrate $[HNO_3 \cdot 3H_2O$ (NAT), the most stable phase] on preexisting H_2SO_4 aerosols (2, 3, 10-15), which produces a unimodal size distribution with a small mean diameter and negligible sedimentation rate (12, 13). Observations often indicate bimodal size distributions (14); most of the vapor condenses onto a few large particles that may grow further to remove HNO₃ by sedimentation (15). The mechanism for initiating differential growth is unclear. Stratospheric measurements often indicate supersaturation of HNO_3 and H_2O vapor relative to NAT (9, 16-20). A proposed mechanism for differential growth assumes that NAT condenses on ice crystals that fall to altitudes where partial pressures of HNO₃ and H₂O exceed equilibrium with NAT (21).

Worsnop et al. (20) reported formation

of metastable nitric acid dihydrate [HNO₃·2H₂O (NAD)] from the vapor phase, even though the saturation ratio $S_{\rm NAT}$ exceeded 10 while $S_{\rm NAD}$ was <3, where S denotes the saturation ratio

 $S_{HNO_3 \cdot jH_2O}$

 $p_{\rm HNO_3}(p_{\rm H_2O})'/K_{\rm HNO_3 \cdot {}_1\rm H_2O}$ (1)

where $K_{\rm HNO_3, iH_2O}$ is the vapor-solid equilibrium constant and P_i is the partial pressure of component *i*. They noted that $S_{\rm NAT}$ would be 3 to 10 in a cloud composed of NAD, consistent with many observations, and that differential growth could result from the conversion of a few NAD particles to NAT. Molina and co-workers (22) studied the uptake of H₂O and HNO₃ by cold H₂SO₄. They suggested that NAT nucleates from the liquid phase when $S_{\rm NAT}$ reaches ~10, causing the supercooled ternary solution to freeze and accrete NAT; Iraci *et al.* (23) formed NAT in this way with a somewhat larger value for $S_{\rm NAT}$ (~400).

We report laboratory studies of HNO₃ hydrates formed from H₂SO₄ and from HNO₃ and H₂O vapor at stratospheric conditions. We identified condensed phases from observations of equilibrium vapor pressures, p_{HNO_3} and p_{H_2O} , measured by tunable diode laser spectroscopy [see figure 1 in (20)], using a multiple-pass Herriot cell (20-m path length) suspended in a thermally insulated, 12-liter ultrahigh-vacuum chamber. We were able to achieve improved detection limits [compare with (20)], better than 5×10^{-8} torr and $5 \times$ 10^{-5} torr for p_{HNO_3} and p_{H_2O} , respectively, by using a single-mode laser and by eliminating the monochromator. A droplet (5 $\mu l)$ of concentrated H_2SO_4 was placed on the temperature-controlled glass button at the bottom of the chamber. We prevented loss of H_2SO_4 by pumping the vacuum

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chamber only when sample temperatures (T_s) were <250 K.

Condensed samples consisted of assemblages of phases, each related to gas-phase vapor pressures by equilibria (24)

K_{aH2SO4}·bHNO3·cH2O

$$= (p_{H_2SO_4})^a \cdot (p_{HNO_3})^b \cdot (p_{H_2O})^c$$
 (2)

where K has units of $torr^{a+b+c}$ and the stoichiometry of the condensed phase (represented by *a*, *b*, and *c*) varies continuously for liquids but takes discrete values for crystals. Equation 2 provides information on crystal composition: for example, in the binary H₂O:HNO₃ solids (a = 0),

$$d(\ln p_{\rm HNO_3})/d(\ln p_{\rm H_2O}) = -n$$
 (3)

(the Gibbs-Duhem relation) where n = c/bmay be determined from the slope of $\ln(p_{\rm HNO_3})$ versus $\ln(p_{\rm H_2O})$ under equilibrium conditions. We determined values of *n* by perturbing the system—for example, by cycling the button temperature (on time scales of hours to days), by briefly opening the chamber to a cryogenic adsorption pump, or by admitting small quantities of HNO₃ or H₂O vapor.

During cooling of the button, phase changes were observed as kinks where discrete changes in *n* produce discontinuities in the first derivative of $\ln(p_{\rm HNO_3})$ versus $\ln(p_{\rm H_2O})$. Identification of *a*, *b*, and *c* from observations of $p_{\rm HNO_3}$ and $p_{\rm H_2O}$ is not possible for an assemblage with a single crystalline phase (because $p_{\rm H_2SO_4}$ could not be measured) unless the crystal is a binary HNO₃ $\cdot j$ H₂O hydrate. However, assemblages of coexisting H₂SO₄–HNO₃–H₂O phases (such as two H₂SO₄–containing crystalline phases) can be identified as shown in Scheme 1, where values of *n* define HNO₃ and H₂O stoichiometry (that is, $K_{\ell-k}$ relations).

Figure 1, A and B, shows the observed decrease in $p_{\rm HNO_3}$ and $p_{\rm H_2O}$ during cooling of the H₂SO₄ droplet from 245 to 192.8 K, reflecting the absorption of HNO₃ and

Scheme 1. Ternary H₂SO₄-HNO₃-H₂O equilibria.

HNO₃-H₂SO₄ hydrates:

NA <i>j</i> :	$K_{\text{HNO3}} = p_{\text{HNO3}} \cdot (p_{\text{H2O}})^{j}$
SAk:	$K_{H_2SO_4, kH_2O} = p_{H_2SO_4} \cdot (p_{H_2O})^k$
MixH:	$K_{H_2SO_4 \cdot mHNO_3 \cdot \ell H_2O} = p_{H_2SO_4} \cdot (p_{HNO_3})^m \cdot (p_{H_2O})^\ell$

Coexisting MixH-SAk [assuming m = 1; see (31)]:

 $K_{\ell - k} = \frac{K_{\mathsf{H}_2 \mathsf{SO}_4 \cdot \mathsf{HNO}_3 \cdot \ell \mathsf{H}_2 \mathsf{O}}}{K_{\mathsf{H}_2 \mathsf{SO}_4 \cdot \mathsf{k} \mathsf{H}_2 \mathsf{O}}} = p_{\mathsf{HNO}_3} \cdot (p_{\mathsf{H}_2 \mathsf{O}})^{\ell - k}$

Coexisting SAk-SAk':

$$\kappa_{k-k'} = \frac{\kappa_{H_2 \text{SO}_4 \cdot k \text{H}_2 \text{O}}}{\kappa_{H_2 \text{SO}_4 \cdot k' \text{H}_2 \text{O}}} = \frac{\kappa_{\ell-k}}{\kappa_{\ell-k'}} = (p_{H_2 \text{O}})^{k-k'}$$

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 H_2O into the liquid. At point 1, a discontinuity in $\ln(p_{HNO_3})/\ln(p_{H_3O})$ indicated formation of a solid phase at stratospheric conditions. The abrupt decrease in p_{HNO_3} with little change in p_{H_2O} implies uptake of HNO₃ by the sample. This formation of an HNO₃ crystalline phase may have been associated with ice formation (as labeled with the blue stars), although ice did not persist (25). The HNO_3 phase was metastable with respect to both NAT and NAD ($S_{NAT} \sim 60$

Fig. 1. Cooling of a 5- μ l drop of H₂SO₄ (95% by weight) in the presence of H₂O and HNO_3 vapor, from 245 to 192.8 K. (A) Relation of $p_{\rm HNO_3}$ and $p_{\rm H_2O}$. Heavy black lines denote the coexistence boundaries for NAD with NAM $HNO_3 \cdot H_2O$ (extreme upper left), NAD with NAT (upper left), and NAT with ice (lower right). The rectangle defines the range of p_{HNO_3} and $p_{H_{2}O}$ in the lower stratosphere. Experimental conditions (such as total H₂O and HNO₃ mass and the cooling rate) were adopted to bring $p_{\rm HNO_3}$ and $p_{\rm H_2O}$ to the upper right corner of the rectangle. The Gibbs-Duhem relations (Eq. 3) are shown for phases given in the legend, for $T_{\rm s}$ = 192.8 K [(20) and Scheme 2]. Symbols denote vapor pressures near equilibrium (S_i = 1 ± 0.1) for phases in the legend; (-) denotes points undersaturated for all listed phases during cooling. (B) Temperature versus day of the year for the experiment, with the same symbols as in (A). Vapor pressures dropped as the sample cooled

and $S_{NAD} \sim 6$). During the several hours of observation, the equilibration of the vapor pressures over the sample followed a $\ln(p_{H,O})$ p_{HNO_3}) ratio with n = 1 (Eq. 3), as demonstrated by the green dotted line in Fig. 1A. However, nitric acid monohydrate (NAM)

could not exist ($S_{NAM} \sim 0.5$). The formation of this HNO₃ phase from the ternary H₂SO₄-HNO₃-H₂O liquid and the Gibbs-Duhem line with n = 1suggest the coexistence of a mixed HNO₃-



(starting at 245 K) for 3 hours, until, at $T_s = 193.5$ K (point 1), the p_{HNO_3}/p_{H_2O} discontinuity indicated crystallization within the liquid. We observed that S_{NAT} peaked at ~80 for a few minutes at point 1. The phase was identified as coexisting MixH:SA4 by n = 1 slope (dotted green line in (A) as in Eq. 3) over the next several hours, as T_s stabilized at 192.8 K. Overnight, NAD formed (point 2); water was added (point 3) to confirm NAD (n = 2, see Eq. 3). NAD persisted for days with repeated small additions of water, with S_{NAT} = 3 to 30. The $p_{H_{2}O}$ fluctuation over ice after point 3 reflects a small fluctuation in T_s (~−0.5 K).

 H_2SO_4 hydrate $[H_2SO_4 \cdot HNO_3 \cdot \ell H_2O$ (MixH)] and a binary H_2SO_4 hydrate $[H_2SO_4 \cdot kH_2O (SAk)]$, with $\ell - k = 1$ (from Scheme 1 and Eq. 3). The variation in $p_{HNO_3}/p_{H,O}$ along the n = 1 line appears to reflect condensation of excess H2O, preferentially growing SAk at the expense of liquid, while maintaining equilibrium with MixH (26).

Figure 2 shows an experiment with somewhat higher initial concentration of water vapor, which initially formed ice at 194 K (point 1); then, NAD formed overnight (point 2), followed by NAT upon warming to 198 K (point 3). The warming curve beyond point 4, after NAT evaporated, exhibited hysteresis compared to the cooling curve [compare with (22, 23)]. Values for p_{H_2O} and the apparent melting point of the H_2SO_4 solid (point 5) are consistent with the presence of sulfuric acid tetrahydrate $[H_2SO_4 \cdot 4H_2O (SA4)]$ and, by the phase rule, a residual liquid phase (27). We never observed formation of the most stable phase (NAT) without prior formation of MixH or NAD, contrary to the sequence usually assumed for PSCs, and the presence of NAD persisted for long periods (as in Fig. 1).

Figure 3 shows evidence for the formation of H_2SO_4 hydrates in three experiments in which the sample was cooled slowly over a period of days. In all three cases, initial discontinuities (points 1, 5, and 8) indicated initial SAk formation $[d(\ln p_{HNO_3})/d(\ln p_{H_2O}) \sim 0]$. Further cooling led to HNO₃ vapor condensation followed overnight by the formation of components consistent with the coexistence of H_2SO_4 hydrates with MixH. For example, in experiment a the liquid ab-

В

274.5

274.5

C

Fig. 2. (A) Relation of $p_{\rm HNO_3}$ and $p_{H_{2}O}$ as in Fig. 1 for cooling from 268 to 192.2 K, then warming to 242 K; (+) denotes points undersaturated with respect to the listed phases during warming. (B) Saturation ratios for binary NAj and coexisting MixH:SAk (see Eq. 3, Scheme 1, and Table 1) versus day of the year. (C) Temperature versus day of the year for the experiment, with the same symbols as in (A). After cooling for 2 hours to $T_s = 195$ K (point 1), ice crystallized and persisted for 1 to 2 hours (but not NAj, even with $S_{\rm NAD}$, $S_{\rm NAT} \gg$ 1). NAD formed overnight (point 2), with $T_s =$



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log(Saturation ratio) -0.2 -0.6 -1.0 272.5 273.0 273.5 274.0 Day 1993 192.2 K. NAT formed on warming to T_s = 197 K (point 3) then evaporated at 207 K (point 4). Higher concentrations of HNO3 and lower concentrations of H2O during warming, as compared to cooling, 220 indicated the persistence of a solid phase of H2SO4 that melted at 236.5 K (point 5), consistent with T(K) $H_2SO_4 \cdot 4H_2O$ (SA4). The points labeled as MixH:SA3 during cool-down (at $T_s = 215$ K) and warm-up 205 (at $T_s = 213$ K) come from coincidental matching of p_{HNO_3} and $p_{H_{2O}}$ with K_{5-3} (25). 190 272.5 273.0 273.5 274.0

1.4

1.0

0.6

0.2

sorbed HNO₃ and H₂O until point 1 at T_s = 207 K, when SAk formation and growth were indicated by the observation that $p_{\rm HNO_3}$ remained constant as SAk grew at the expense of the residual ternary liquid. At point 2, p_{HNO} , decreased, consistent with MixH formation. Another discontinuity at point 3 indicated a transition from one sulfuric acid hydrate (SAk) to another (SAk'), still coexisting with MixH. The overnight points (subsequent to points 2 and 3) were consistent with coexisting MixH and SAk with $\ell - k = 2$ and 3, and the presence of SAk was confirmed by hysteresis upon warming. Experiments b and c followed similar patterns, with different values of $\ell - k$.

Kinks such as those shown in Fig. 3 were repeatedly observed in more than 20 cooling experiments performed over the temperature

Table 1. Equilibrium constants for assemblages of ternary phases (InK = A/T + B); ΔS^{o} and ΔH^{o} are, respectively, the standard entropy and enthalpy, and *R* is the gas constant. Thus, $\Delta S^{o}/R = B - n \ln(760)$; where *K* has units of torr^{*n*}, and $\Delta H^{o}/R = -A$.

Constant	x – y	Units	∆Sº/R	∆H⁰/R
K _{ℓ-k}	$ \begin{cases} 5-4 \\ 5-3 \\ 5-2 \end{bmatrix} $	Torr² Torr³ Torr⁴	74.38 92.43 110.74	21251 28375 35533
$K_{k-k'}$	{ 4-3 3-2	Torr Torr	18.05 18.31	7124 7158
$K_{\text{HNO}_3 \cdot 3\text{H}_2\text{O}}$	(α)	Torr⁴	79.16	28474

Fig. 3. Slow cooling and warming experiments (symbols as in Figs. 1 and 2): experiment a, 236 to 191.5 to 202 K; experiment b, 253 to 186.4 K; experiment c, 227 to 190.7 to 209 K. (A) Relation of p_{HNO_3} and $p_{H_2O_2}$. (B) Temperature versus day of the year. (C) Saturation ratios for experiment a, as in Fig. 2B. During cooling in all three experiments, the first discontinuity $[d(\ln p_{HNO_3})/d(\ln p_{H_2O}) \sim 0]$ indicated binary SAk formation (points 1, 5, and 8 in experiments a, b, and c, respectively). The point in experiment b labeled as MixH:SA3 at $T_{\rm s} = \sim 198$ K after point 5 is a coincidental matching of $p_{\rm HNO_3}$ and $p_{\rm H_{2O}}$ with K_{5-3} (25).] In experiments a and b, MixH formed at points 2 and 6, respectively, identified in coexistence with SAk: (a) k =2: (b) k = 4. In experiment a. SA3 then formed (point 3), whereas in experiment b SA4 persisted (point 7). In experiment c, α -NAT formed at point 9, then disappeared when ice formed at point 10; NAD later nucleated at point 11 after warming.

range $T_s = 192$ to 205 K (28). Phase assemblages involving $H_2SO_4 \cdot HNO_3 \cdot 5H_2O$ co-existing with SA4, $H_2SO_4 \cdot 3H_2O$ (SA3), and $H_2SO_4 \cdot 2H_2O$ (SA2) were identified (also possibly $H_2SO_4 \cdot H_2O_3$, in a single experiment) (29). For experiment a in Fig. 3, the identification of $\ell - k$ is illustrated in Fig. 3C, which shows the saturation ratios for different phase assemblages. The overnight points following points 2 and 3 occur at pressures too low for either MixH:SA4 or any binary NAj hydrate. Nevertheless, discontinuities clearly indicated PHNO1 MixH formation. The low values for $p_{H_{2O}}$ would be expected to favor $H_2SO_4 \cdot kH_2O$ with smaller values of k, as identified.

Results are summarized in Fig. 4, which shows observations of K_{ℓ} and $K_{\ell-k}$ versus T_s^{-1} for every observed discontinuity for all experiments. The integer values found for *a*, *b*, and *c* for the ternary phases (see Eq. 2) are related to ratios of H₂SO₄/HNO₃/H₂O equilibrium constants. We inferred values of *m* and ℓ for MixH (see Scheme 1) by comparing our data with the H₂SO₄ · *k*H₂O phase diagram [see discussion in (30)] in which k =2, 3, and 4 and with known melting points of H₂SO₄ · *k*H₂O phases (31).

This analysis is corroborated by consideration of coexisting $H_2SO_4 \cdot kH_2O$ phases (SAk:SAk'), which equilibrate with a unique $p_{H,O}$ at fixed T_s (that is, $K_{k-k'} = (p_{H_2O})^{k-k'}$; see Scheme 1). As illustrated in Fig. 5, which plots $K_{k-k'}$ lines derived from ratios of our experimental $K_{\ell-k}$ relations (see Scheme 1), our values for p_{H_2O} reproduce measurements from Zhang *et al.* (30) for coexisting SA4:SA2. It should be emphasized that Fig. 5 plots $K_{k-k'}$ values that represent independently derived, absolute values of $p_{\rm H_{2}O}$ as a function of T. The similarity of K_{4-3} and K_{3-2} , which correspond to the "steps" in overnight equilibria after points 2 and 3 in Fig. 3A, confirm the similarity in the heats of vaporization (30). Table 1 summarizes our thermodynamic



Fig. 4. Plot of K_{a-b} ratios (see Scheme 1) versus 1/*T*. Points refer to all experimental points that equilibrated for more than an hour for more than 20 experiments, with phases (or assemblages) identified either from the line with constant *n* (Eq. 3) or from $d(\ln p_{\rm HNO_3})/d \ln p_{\rm H_{2O}})$ discontinuities as discussed in the text. Equilibrium constants for NAT and NAD are taken from (20); other lines represent fits to the data (see Scheme 2). Metastable α -NAT was identified as an n = 3 phase that sometimes formed with $K_3 > K_{\rm NAT}$ (33), consistent with the identification by Koehler *et al.* (32).



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results for MixH:SAk and SAk:SAk' equilibria (giving K_{x-y} ratios as defined in Scheme 1), as well as the equilibrium constant for an n = 3 phase identified as α -NAT, a metastable form of NAT observed in thin-film studies (31–33). Scheme 2 lists ternary phases likely to be formed in the stratosphere, in more or less increasing order of stability (relative stability is a complex function of temperature and vapor pressure).

The observed formation and persistence of metastable phases (MixH and NAD) at stratospheric temperatures and vapor pressures strongly suggest that PSC formation is influenced by a complex ternary H₂SO₄-HNO₃-H₂O phase diagram, in contrast to the common view of PSC formation by simple NAT nucleation [compare with (22, 23)]. In all our experiments, NAT was the last phase to form, even with $S_{NAT} > 10$, often appearing only on a time scale of days (34). Formation of NAD was preferred, in association with mixed and binary H_2SO_4 hydrates (35). Even when large values of p_{H_2O} led to ice nucleation (as in Fig. 2), NAD formed first, with NAT appearing only after subsequent warming.

Ostwald's rule (36, 37) states that as a solution is cooled, the first phase to form



Fig. 5. Plot of $K_{k-k'}$ ratios for coexisting SAk: SAk' hydrates (see Scheme 1) versus 1/T, with lines from fits to our data. Points (x) for SA4:SA2 coexistence are from Zhang *et al.* (30) (our SA4: SA2 line lies midway between the plotted SA4: SA3 and SA3:SA2 lines). Nearly overlapping lines reflect similar free energy for water vaporization for various SAk hydrates. The T_s range of 192 to 205 K for our $K_{\ell-k}$ observations extrapolates to the data of Zhang *et al.* (30) for T = 198to 222 K.

Scheme 2: Possible H2SO4-HNO3-H2O ph	nases
in the stratosphere.	

Liquid:	H₂SO₄·HNO₃·H₂O
Solid:	H₂SO₄·HNO₃·5H₂O
	H₂SO₄·2H₂O (SA2)
	H ₂ SO ₄ ·3H ₂ O (SA3)
	$H_{2}SO_{4} \cdot 4H_{2}O$ (SA4)
	HNO3 2H2O (NA2)
	HNO3 3H2O (NA3)
	H ₂ O

will often be the least stable that is thermodynamically accessible. This rule is invoked to explain formation of supercooled water clouds in the atmosphere (36) and to help select quenching rates in metallurgical applications (37). According to Turnbull (37), low barriers to nucleation of metastable phases result from general trends in surface free energies, which inversely correlate with crystal free energies. We find that the ternary system follows Ostwald's rule (38). The inferred composition for MixH ($H_2SO_4 \cdot HNO_3 \cdot 5H_2O$) is near to that of the liquid melt for stratospheric conditions, implying relatively little rearrangement to form a crystal and perhaps explaining its apparently low barrier to nucleation. All of these phases, including metastable $H_2SO_4 \cdot kH_2O$, may be formed in coexistence with residual ternary liquid solutions under stratospheric conditions (27, 39).

Observations of PSCs have led to the postulation of diverse mechanisms for their microphysical development. Many of these observations are consistent with the behavior predicted from the phases shown in Scheme 2 and Ostwald's rule (9, 17-19). For example, in a Type I PSC in the Arctic (18), large particles appeared at 193 K ($S_{NAT} \sim 10$) rather than at 195 K (where $S_{NAT} \sim 1$), and volumes increased uniformly as temperatures declined below 193 K. The data are consistent with NAD particles (S $_{\rm NAD} \sim 1$ at 193 K) but inconsistent with NAT: if made of NAT, particle volumes either should begin to increase at S_{NAT} \sim 1 or, if nucleation is inhibited, should increase discontinuously once nucleation occurs. Observed differential growth of the particles (36) can also be explained by Ostwald's rule: MixH could form first and stochastically transform to NAD, with the first particles to convert acquiring the most particle mass. These solid phases may often coexist with a ternary liquid solution in the stratosphere (39), which would explain the absence of depolarization in lidar observations (40).

We have argued (20, 21) that the tendency for differential growth of PSCs is a consequence of the formation of metastable phases. In this report we identify a probable initial phase as a previously unknown hydrate of HNO₃ and H₂SO₄ and show that NAD is probably an important, persistent phase for condensed HNO₃ in PSCs. The key to understanding denitrification of the polar stratosphere and the associated "ozone hole" phenomenon is to define the influence of environmental conditions (cooling rates, temperature fluctuations, and initial aerosol size distributions) on the formation and growth of metastable phases and their transformation to more stable phases.

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- 25. Data points are labeled with symbols (such as the blue star for ice in Fig. 1 after point 1) if $p_{H_{2O}}$ and $p_{H_{NO_3}}$ match the equilibrium for a phase assemblage (defined by K_{x-y} in Scheme 1 and Table 1) as measured by $S_r = 1 \pm 0.1$. Such a criterion does not in itself prove the presence of a phase. Particularly during cool-down and warm-up (see Fig. 2), coincidental matching of $p_{H_{2O}}$ and $p_{H_{NO_3}}$ with $S_r \sim 1$ can occur. Reliable phase identification is associated with $d(\ln p_{H_{NO_3}})/d(\ln p_{H_{2O}})$ discontinuities and persistence of equilibrium for a few hours, especially overnight. Data points with coincidental $S_r \sim 1$ matching are noted in Figs. 2 and 3.
- 26. The cool-down time of about 2 hours for this experiment (Fig. 2) was much faster than the ~1-day equilibration time for diffusion within the liquid sample at T < 200 K, leading to an inhomogeneous liquid composition below the surface. Relaxation of these inhomogeneities likely moved the system along the n = 1 line in Fig. 1.
- 27. A wholly frozen droplet would have to contain two hydrates of H₂SO₄ (such as H₂SO₄ · 4H₂O + H₂SO₄ · 6.5 H₂O); p_{H_2O} would lie on their coexistence boundary, giving a unique p_{H_2O} for a given T_s (see $K_{k-k'}$ in Scheme 1 and Fig. 5).
- 28. For binary SAk and ternary MixH hydrates coexisting with a ternary liquid, the phase rule constrains p_{H2O} and p_{HNO3} to unique values for fixed T_s. The usual observation of MixH:SAk coexistence as

kinks (see Fig. 3) reflects liquid-solid coexistence points at a given temperature and composition.

- 29. We may have observed the hemihexahydrate as well; however, it is favored at high p_{H2O}/p_{HNO3} ratios where ice nucleation tended to complicate metastable phase identification.
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- 33. This α-NAT phase was identified from slightly high K_{HNO3} · 3H₂O values that were observed only during initial nucleation of NAT, usually converting to NAT overnight, consistent with overall phase formation by means of metastable phases. Such a metastable form of NAT is consistent with α-NAT identified by Koehler *et al.* (32) and also observed by Iraci *et al.* in liquid H₂SO₄ films (23).
- 34. The only exception is experiment c in Fig. 3, when slow cooling led to the initial formation of metastable α-NAT. However, even in that experiment the α-NAT did not persist, with subsequent ice nucleation leading to metastable NAD.
- 35. The current experiment is extremely sensitive to metastable phases. Detection of the vapor phase allows a gas-solid equilibrium to be maintained by a thin surface layer (tens of monolayers or less), minimizing the saturation ratios required for phase formation and growth. Metastable phases are easily

detectable with our capability for long observationequilibration times. Thus, our observations of sequential phases forming in the ternary system are not necessarily inconsistent with recent reports of direct NAT nucleation from the ternary liquid (22, 23). Those experiments detected relatively large crystals difficult to grow under equilibrium conditions.

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- Supported by the National Aeronautics and Space Administration: Upper Atmospheric Research Program, contract NASW 4126, and Atmospheric Effects of Aircraft Program, contract NAS1-19931, both to Aerodyne Research.

19 July 1994; accepted 5 October 1994

Mechanisms of Argon Retention in Clays Revealed by Laser ⁴⁰Ar-³⁹Ar Dating

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A method for dating clays is important for studies of weathering, diagenesis, hydrocarbon migration, and the formation of major metalliferous deposits. However, many attempts have produced imprecise or inaccurate results. Data from shales show that, contrary to expectations, the ⁴⁰Ar-³⁹Ar dating technique can be successfully used to determine the diagenetic age of ancient sediments because ³⁹Ar losses during irradiation are controlled by release from low retentivity sites in illite equivalent to those that have lost radiogenic ⁴⁰Ar in nature, rather than by direct recoil as is generally assumed.

Formation of clavs involved in weathering, diagenesis, or hydrothermal alteration has been difficult to study because such low temperature nonequilibrium processes are difficult to simulate experimentally. Clay mineral diagenesis has been variously ascribed to progressive temperature-induced formations (1), fluid mediated punctuated recrystallization (2, 3), and Ostwald ripening (4). In order to test these hypotheses, or establish the ages of diagenetic and hydrothermal reactions in nature, suitable isotopic dating methods must be developed for determining the timing of clay mineral growth. This has not been straightforward. The Rb-Sr approaches (2, 3) are generally limited by concerns over the uniformity of initial isotopic composition. Sm-Nd methods (3, 5) have similar problems and lack precision. K-Ar dating (6) is limited by the uncertainties of Ar loss. Furthermore, all of these techniques must utilize reasonably large samples (> 10 mg).

The ⁴⁰Ar-³⁹Ar dating technique is a potentially powerful method for dating clay diagenesis and low-grade metamorphism because it can easily be applied to small samples and, with step-heating, allows one to see through the effect of Ar loss. However, despite early attempts (7, 8), it has long been known that during irradiation, ³⁹Ar is lost from fine-grained samples such as clays (9-13), rendering the apparent ages meaningless. The recoil distance of ³⁹Ar has been estimated to be 0.08 μ m (9), the same magnitude as the typical grain sizes of clay minerals (14). Comparisons with conventional K-Ar determinations (12) and experiments with quartz tube encapsulation

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(15–17) indicate sizable losses of ³⁹Ar, up to 60%, during irradiation. However, some comparisons between K-Ar and ⁴⁰Ar-³⁹Ar ages in fine-grained clay-like minerals yielded concordant results (12, 18–20), suggesting that under some circumstances, ³⁹Ar loss due to recoil is negligible. Indeed, it has been inferred that the extent of ³⁹Ar loss can be a function of the nature $\tilde{o}f$ clay grain boundaries and the relationships with neighboring grains (12, 18).

Illite, the most common K-rich clay mineral, commonly forms by diagenetic alteration of smectite, and in many sedimentary rocks, clays consist of mixed layers of these two minerals. Transmission electron microscopy (TEM) observations of illitesmectite (I-S) mixtures from mudstones (21) have revealed a positive correlation between the proportion of smectite-like layers and the relative proportions of imperfections in I-S crystallites. These imperfections may serve as pathways for radiogenic ⁴⁰Ar diffusion loss in nature or the laboratory and ³⁹Ar loss in the reactor. In this study we address the relation between the proportion of imperfections in I-S clays and the extent of Ar recoil-diffusion loss with a combination of TEM observations and vacuum encapsulation experiments on submilligram samples of clays.

We initially analyzed two bentonites and one shale from the classic Lower Paleozoic sedimentary successions of Wales. These horizons have well-established biostratigraphy and their depositional ages have been determined or bracketed by U-Pb zircon dating of bentonites (22). The shale has been independently studied using Rb-Sr and Sm-Nd techniques (5, 23). A similar experiment was performed on a well-characterized siltstone sample, also primarily studied by TEM, Rb-Sr, and Sm-Nd, from the Onondaga Group (Middle Devonian) of upper New York State. Bentonite sample RIM536 is from the Middle Cambrian Menevian Beds with a depositional age of 517 to 530 Ma (24). However, it was significantly metamorphosed during the Acadian orogeny at about 397 Ma (23), as indicated by its small illite crystallinity value of 0.17 (epizone). Bentonite sample BRM1311 is from the Upper Caradoc Formation (Ordovician) and has a depositional age range of 443 to 462 Ma (24). As opposed to RJM536, it is of low grade with an illite crystallinity (IC) of 0.84, corresponding to diagenetic grade. Three size fractions (5 to 1 μ m, 1 to 0.2 μ m, and <0.2 μ m) were obtained from the diagenetic shale collected from Pwllheli in the Welsh Basin. It has a depositional age within the range 461 to 449 Ma (5). The same size fractions were used for the diagenetic siltstone from New York. It has a maximum depositional age of 390 \pm 1 Ma (5) determined from

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