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SOM Text

Fig. S1

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# Atmospheric New Particle Formation Enhanced by Organic Acids

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Atmospheric aerosols often contain a substantial fraction of organic matter, but the role of organic compounds in new nanometer-sized particle formation is highly uncertain. Laboratory experiments show that nucleation of sulfuric acid is considerably enhanced in the presence of aromatic acids. Theoretical calculations identify the formation of an unusually stable aromatic acid–sulfuric acid complex, which likely leads to a reduced nucleation barrier. The results imply that the interaction between organic and sulfuric acids promotes efficient formation of organic and sulfate aerosols in the polluted atmosphere because of emissions from burning of fossil fuels, which strongly affect human health and global climate.

Aerosols influence the Earth-atmosphere system in several distinct ways (1, 2). Concerns over the human health effects of fine particulate matter constitute the most important element in formulating the national ambient air quality standard (3). Also, aerosols directly or indirectly affect the Earth's radiation budget (4, 5), and light absorption by aerosols causes visibility degradation. Furthermore, modification of clouds and precipitation by aerosols may enhance lightning activity and thus influence tropospheric chemistry (6, 7). The impacts of particulate matter on health, radiation, and cloud microphysics are strongly dependent on the particle sizes.

Several processes determine the aerosol size distribution, including new particle production (as a result of gas-to-particle conversion), growth due to condensation and coag-

ulation, removal rates, and primary emissions. New particle formation or nucleation is the least understood of these steps (8). Much of the previous research has focused on nucleation of sulfuric acid, because sulfate represents an important component of the nucleation mode aerosol (9). It is commonly recognized that binary nucleation of H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub> is not efficient enough to explain atmospheric new particle formation (10). Progress recently has been made in assessing the importance of ternary water–sulfuric acid–ammonia nucleation (11, 12), ion-induced nucleation (13, 14), and nucleation involving iodide species (15, 16).

The role of organic compounds in new particle formation is another potentially important issue (17). Atmospheric measurements reveal that aerosols often contain a considerable amount of organic matter (18–21). During photooxidation of volatile organic compounds (VOCs), non- or semivolatile organic products are produced that contribute to secondary organic aerosol (SOA) formation. For example, in the urban atmosphere the aromatic component in gasoline (mainly toluene and xylenes) is responsible for SOA formation caused by oxidation of these com-

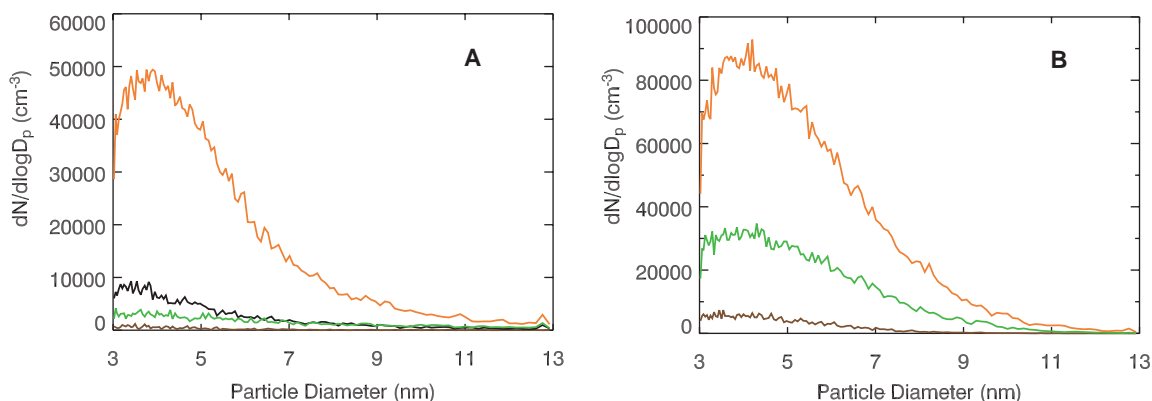
pounds (22). Current theory of SOA formation assumes that condensation of low-volatility organic species such as carboxylic or dicarboxylic acids occurs on preexisting particles from primary emissions or formed by homogeneous nucleation, most probably involving sulfuric acid–ammonia–water or ions (8). Alternatively, it is suggested that SOA nucleation may occur through the formation of stable organic heterodimers (23). Currently, few experimental studies have investigated new particle formation from organic acids. Another process, which also influences the chemical composition of organic aerosols, involves absorption of gaseous species onto particulate matter. On the basis of consideration of the thermodynamic equilibrium distribution of a compound between the gas and condensed phases, a gas–particle partitioning model has been proposed (24) and invoked to explain the observed correlation between the SOA yield and the organic aerosol mass concentration (22, 25). More recently, it has been suggested that sulfate aerosols catalyze heterogeneous reactions of carbonyl compounds, leading to a considerably enhanced SOA yield (26). The growth of SOA from both mechanisms depends on preexisting particles, which are linked to new particle formation or primary emissions.

To assess the role of low-volatility organic species in new particle formation, we performed laboratory studies of particle nucleation from aromatic acid vapors and their mixtures with H<sub>2</sub>SO<sub>4</sub> (27). Aromatic acids, such as benzoic (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>), *p*-toluic (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>), and *m*-toluic (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>) acids, are products from photochemical degradation of aromatic hydrocarbons emitted from automobiles in the urban atmosphere (28) and have been identified in the particle phase (29, 30). Nanometer-sized particles were produced in an aerosol chamber, and the particle concentration and size distribution were monitored with an ultrafine particle counter (model 3025A, TSI Incorporated Particle Instruments, St. Paul, MN) and a nanodifferential mobility analyzer (model 3085, TSI Incorporated Particle Instruments) capable of measuring particle

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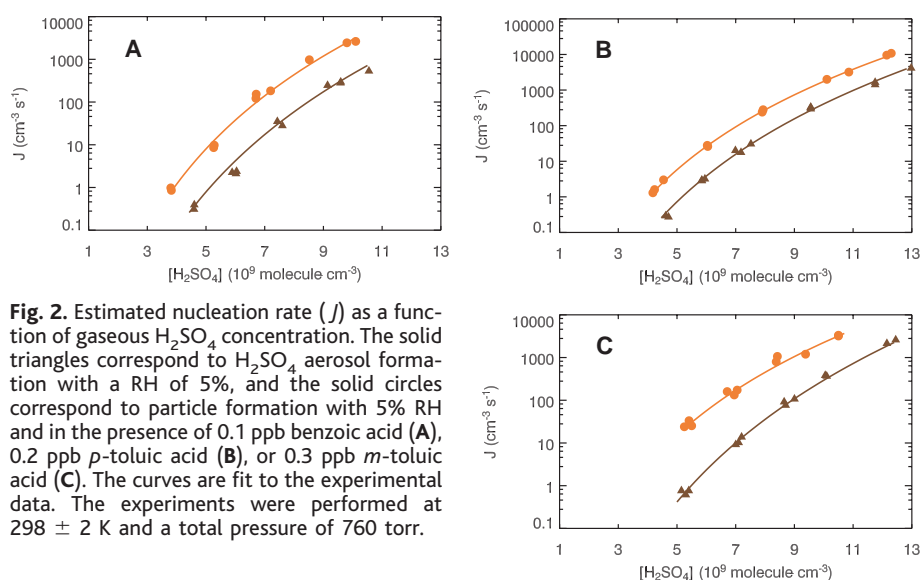
**Fig. 1.** Measured particle size distributions of the nucleating aerosols. In (A), the brown and black curves correspond to  $\text{H}_2\text{SO}_4$  aerosol formation with a RH of 5% and gaseous  $\text{H}_2\text{SO}_4$  concentrations of  $6 \times 10^9$  and  $8 \times 10^9$  molecule  $\text{cm}^{-3}$ , respectively. The green and orange curves are similar to the brown and black curves, respectively, except for addition of 0.04 ppb benzoic acid to the aerosol chamber. In (B), the brown curve corresponds to  $\text{H}_2\text{SO}_4$  aerosol formation with a RH of 5% and a gaseous  $\text{H}_2\text{SO}_4$  concentration of  $7 \times 10^9$  molecule  $\text{cm}^{-3}$ . The green and orange curves are similar



to the brown curve, except for the addition of 0.04 and 0.1 ppb benzoic acid (corresponding to  $1 \times 10^9$  and  $2.5 \times 10^9$  molecule  $\text{cm}^{-3}$ ), respectively. The experiments were performed at  $298 \pm 2$  K and a total pressure of 760 torr.

sizes as small as 3 nm (fig. S1). Gas-phase concentrations of the organic and sulfuric acids in the aerosol chamber were monitored with the use of proton-transfer reaction mass spectrometry and chemical ionization mass spectrometry, respectively (31, 32). We initially generated  $\text{H}_2\text{SO}_4$  aerosols by introducing gas-phase  $\text{H}_2\text{SO}_4$  in a nitrogen carrier gas with a variable relative humidity (RH). For a gaseous  $\text{H}_2\text{SO}_4$  concentration in the range of  $10^9$  to  $10^{10}$  molecule  $\text{cm}^{-3}$ , the particle sizes formed ranged from 3 to 10 nm (Fig. 1), corresponding to the nucleation mode. The observed particle concentration increased when the gaseous  $\text{H}_2\text{SO}_4$  concentration or RH was increased. A marked increase in the particle concentration occurred when benzoic acid vapor was added to the aerosol chamber (Fig. 1). With  $\text{H}_2\text{SO}_4$  concentrations of  $6 \times 10^9$  and  $8 \times 10^9$  molecule  $\text{cm}^{-3}$ , addition of 0.04 ppb (parts per billion) benzoic acid increased the particle concentration by a factor of 5 (Fig. 1A). For a fixed  $\text{H}_2\text{SO}_4$  concentration, higher amounts of benzoic acid resulted in more pronounced particle formation (Fig. 1B). Figure 1 shows that the measured peak diameter of the particle distribution shifted slightly to a larger size with addition of benzoic acid, implying that the presence of benzoic acid both enhanced nucleation and contributed to the growth of the newly nucleated particles. Substantially larger peak diameters ( $>10$  nm) were detected when benzoic acid concentrations were increased by one to two orders of magnitude.

The aerosol nucleation rate,  $J$ , was estimated on the basis of the ratio of the measured particle concentration to the nucleation time (33). In the absence of organic acids, the nucleation rate is dependent on the gas-phase  $\text{H}_2\text{SO}_4$  concentration and RH. Our measured nucleation rate of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  binary system is qualitatively in agreement with previous experimental



**Fig. 2.** Estimated nucleation rate ( $J$ ) as a function of gaseous  $\text{H}_2\text{SO}_4$  concentration. The solid triangles correspond to  $\text{H}_2\text{SO}_4$  aerosol formation with a RH of 5%, and the solid circles correspond to particle formation with 5% RH and in the presence of 0.1 ppb benzoic acid (A), 0.2 ppb *p*-toluic acid (B), or 0.3 ppb *m*-toluic acid (C). The curves are fit to the experimental data. The experiments were performed at  $298 \pm 2$  K and a total pressure of 760 torr.

studies (12). Figure 2 shows that the nucleation rate was considerably increased in the presence of the organic acids. The nucleation rate in the presence of 0.1 ppb benzoic acid is about a factor of 8 to 10 higher than that of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  binary system. Enhanced nucleation rates were also observed for *p*-toluic and *m*-toluic acids (Fig. 2, B and C). The nucleation rate was increased by a factor of 5 to 13 in the presence of 0.2 to 0.3 ppb of the two acids. For RH in the range of 4 to 15%, addition of sub-ppb levels of the aromatic acids consistently led to a larger nucleation rate by a factor of 5 or higher than that of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  binary system (fig. S2). The partial pressures of the aromatic acids in those experiments were several orders of magnitude smaller than their corresponding equilibrium vapor pressures; that is, the saturation ratio,  $S$  (34), was much smaller than unity. Interestingly, the high nucleation rate was also measured in the absence of water vapor for benzoic acid and *p*-toluic

acid, indicating that binary nucleation of the organic acid-sulfuric acid system is responsible for the enhanced new particle formation (35). Hence, these results suggest a probable interaction between the aromatic acid and sulfuric acid that leads to a reduced (heteromolecular) nucleation barrier. The magnitude of the effect of aromatic acids on  $\text{H}_2\text{SO}_4$  nucleation enhancement appears to be comparable to that previously reported for ammonia at similar  $\text{H}_2\text{SO}_4$  and ammonia additive concentrations and RH (fig. S3).

We also examined (homomolecular) nucleation of the aromatic acids in the absence of sulfuric acid and water. New particle formation was only detected when a substantial saturation ratio was established in the aerosol chamber. The minimum  $S$  required to produce detectable new particles was about 45 for benzoic acid and even higher for *p*-toluic and *m*-toluic acids. Similarly, water was observed to have a negligible influence on the organic particle formation for benzoic and *p*-toluic acids,

**Table 1.** Bonding energies,  $D_0$  (in kcal mol<sup>-1</sup>), of the aromatic acid–sulfuric acid complexes. BA-SA denotes benzoic acid–sulfuric acid complex; PTA-SA, *p*-toluic acid–sulfuric acid complex; and MTA-SA, *m*-toluic acid–sulfuric acid complex. All energies are corrected with the zero-point energies (ZPE). The quantum chemical methods used in the present study are similar to those used by Suh *et al.* (28).

Complex	$D_0$
BA-SA	19.85*
	17.62†
	18.63‡
	17.84§
PTA-SA	19.99*
MTA-SA	23.72*

\*Determined with B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p). †Determined with CCSD(T)/6-31G(d) + CF//B3LYP/6-31G(d,p). ‡Determined with QCISD(T)/6-31G(d)//MP2(full)/6-31G(d). §Determined with G2(MP2, SVF).

because the two organic acids are insoluble in water and the organic aerosols formed are hydrophobic. In general, particle formation can be qualitatively predicted in terms of fundamental thermodynamic and kinetic principles (36). The spontaneous gas-to-particle conversion process corresponds to a decreased free energy and is thermodynamically favorable but kinetically hindered. During nucleation, a thermodynamically stable cluster or critical embryo is generated before condensation growth of the particle, and this embryo formation involves an energy barrier. Also, condensation growth of nucleated critical embryos will be retarded because of increased activity due to the Kelvin barrier. Hence, particle nucleation and subsequent growth in a single-component system occur only if the system is supersaturated ( $S > 1$ ). It is conceivable that large barriers generally exist for other carboxylic or dicarboxylic acids, as shown in our experiments for the aromatic acids. The atmospheric concentrations of the low-volatility organic compounds are typically at the ppb level or less, even under polluted conditions (1, 2). Although certain dicarboxylic acids do reach their saturation points in the atmosphere (18), the high supersaturation required for homomolecular nucleation likely renders new particle formation from those compounds implausible. Previous smog chamber studies reported homogeneous nucleation from low-volatility organic compounds, but those experiments were carried out with the use of hydrocarbon concentrations that were several orders of magnitude higher than those found under the ambient conditions (25).

To gain an insight into the nature of the interaction between aromatic and sulfuric acids at the molecular level, we performed quantum chemical calculations that show the formation of surprisingly stable aromat-

ic acid–sulfuric acid complexes (fig. S4). The equilibrium aromatic acid–sulfuric acid structure exhibits a nearly planar eight-membered ring: There are two hydrogen bonds, with the organic acid molecule acting as both a hydrogen bond donor and acceptor. The strength of the hydrogen bonding is reflected by the calculated bond lengths. For the benzoic–sulfuric acid complex, for example, the hydrogen bond is 1.503 Å for C=O...HOS and 1.705 Å for COH...O=S, nearly comparable to weak covalent bonds. The energetics of the complexes was quantified with a series of quantum chemical calculations (Table 1). The bonding energies of the complexes are about 20 kcal mol<sup>-1</sup> for benzoic and *p*-toluic acids and are about 4 kcal mol<sup>-1</sup> higher for *m*-toluic acid. For comparison, the bonding energy is about 10 kcal mol<sup>-1</sup> for the H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub> complex (37) and 25 kcal mol<sup>-1</sup> for the H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub>–NH<sub>3</sub> system (38). The large stability of the organic acid–sulfuric acid complex implies that the aromatic acid molecule bonds irreversibly to H<sub>2</sub>SO<sub>4</sub> under atmospheric conditions. The complex formation between aromatic and sulfuric acids most likely reduces the barrier in heteromolecular nucleation and helps condensation growth of the nucleated critical embryo by overcoming the Kelvin effect, explaining the enhanced new particle formation observed in our experiments. Additional calculations were performed for glutaric acid, indicating that stable complex formation with sulfuric acid represents a general feature for organic compounds with the carboxylic or dicarboxylic functional group. It is likely, though, that for smaller organic acids the effect on H<sub>2</sub>SO<sub>4</sub> nucleation may be less important than that observed for the aromatic acids (39).

Organic acids have been widely identified as common components in atmospheric particulate matter (18–21). Our experimental study shows that homomolecular nucleation of aromatic acids is unlikely to occur under atmospheric conditions, but that the interaction between aromatic acids and sulfuric acid promotes efficient heteromolecular nucleation. The gas-phase concentration of organic acids is substantially higher than that of gaseous H<sub>2</sub>SO<sub>4</sub> in the atmosphere (18); thus, organic acids can also contribute considerably to the initial growth of the newly nucleated embryos, which is important for subsequent particle growth by adsorption or heterogeneous reactions of other organic vapors. The particle formation mechanism proposed in this study can have major implications for SOA and sulfate aerosol formation in polluted areas, because both organic and sulfuric acids are photochemical degradation products linked to the emissions from the burning of fossil

fuels (1, 2). In particular, new particle formation can occur efficiently over a large portion of northern America, eastern Asia, and some parts of central Europe because of the concurrent anthropogenic VOC and SO<sub>2</sub> emissions in those regions (fig. S5) (40). Our results suggest an alternative cause for efficient aerosol nucleation frequently observed in the polluted atmosphere, in addition to the available theories of water–sulfuric acid–ammonia ternary nucleation and ion-induced nucleation. For example, enhanced new particle formation (with a particle size of 3 to 4 nm) was observed in anthropogenic plumes advecting from Asia, which were identified by elevated CO and SO<sub>2</sub> concentrations (41). The high CO amount was indicative of the abundance of VOCs inside those plumes. It was speculated that a high SO<sub>2</sub> concentration, in conjunction with other unidentified, possibly co-emitted species, was responsible for nucleation. In contrast, the same study revealed that few 3- to 4-nm particles were detected in the clean background and even within a volcanic plume that had a high H<sub>2</sub>SO<sub>4</sub> but low CO concentration. Also, measurements of aerosol hygroscopicity during the 1999 Houston Supersite Project indicated a dominance of the organic matter in the fine particle mode, which could not be explained by the formation of ammonium sulfate (21). Those measurements likely can be explained by the importance of organic acids in particle nucleation and growth in the presence of sulfuric acid, because of the large abundance of both types of acids in urban environments and in the tropospheric boundary layer influenced by anthropogenic pollution.

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33. The nucleation rate is more precisely defined as the rate at which particles of critical size are produced. In this study, we detect only particles larger than 3 nm, and hence the value estimated from the rate of observed particle formation may be smaller than that of cluster formation.
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39. The bonding energy of complexes represents one of the factors that determine particle nucleation. Other physicochemical parameters, such as the surface tension and equilibrium vapor pressures of the nucleated single or multicomponent system, also influence new particle formation. For example, our experimental results indicated a negligible effect of glutaric acid ( $C_5H_8O_4$ ) on sulfuric acid nucleation, although the bonding energy of this organic acid with sulfuric acid is  $19.2 \text{ kcal mol}^{-1}$ , comparable to those of the aromatic acid-sulfuric acid complexes.
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## Supporting Online Material

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Figs. S1 to S5

References

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# The Acquisition of Exogenous Algal Symbionts by an Octocoral After Bleaching

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Episodes of coral bleaching (loss of the symbiotic dinoflagellates) and coral mortality have occurred with increasing frequency over the past two decades. Although some corals recover from bleaching events, the source of the repopulating symbionts is unknown. Here we show that after bleaching, the adult octocoral *Briareum* sp. acquire dinoflagellate symbionts (*Symbiodinium* sp.) from the environment. Uptake of exogenous symbionts provides a mechanism for response to changes in the environment and resilience in the symbiosis.

A diverse array of cnidarians form symbioses with photosynthetic dinoflagellates in the genus *Symbiodinium*. These are true mutualisms, in that the symbiont receives inorganic nutrients from the host and the host obtains translocated photosynthetic products from the symbionts (1–3). Symbiont species within the diverse genus *Symbiodinium* are classified into broad groups or clades (i.e., A, B, C, etc.) on the basis of sequence variation in the small-subunit ribosomal gene (4–6). Most cnidarians preferentially establish and maintain a stable symbiosis with either a specific clade of *Symbiodinium* (7–10) or a subset of the clades that vary with environmental gradients such as light intensity (11–14). Environmental perturbation (e.g., increased temperature, increased solar radiation) can result in the breakdown of the symbiosis (i.e., coral bleaching) that can lead to coral death and subsequent reef degradation. However, some corals recover, and bleaching has been posited as a mechanism whereby hosts acquire new, potentially better-adapted symbionts (4, 15, 16). The source of the symbionts that repopulate a host colony following bleaching is poorly understood (11, 16, 17). Are the symbionts derived from *Symbiodinium* populations remaining in the host at very low levels or from an exogenous pool of potential symbionts (12, 17–19)?

To determine whether adult corals can acquire exogenous symbionts from the environment after a bleaching event, the Caribbean octocoral *Briareum* sp. was bleached and then exposed to exogenous *Symbiodinium* containing rare variants of the chloroplast 23S ribosomal DNA (rDNA) domain V region (cp23S-genotype) (20). The potential symbionts were derived from isoclonal lines of *Symbiodinium* clade B initially isolated from newly settled octocoral polyps (cp23S-genotypes B211 and B223) and an adult col-

ony of *Plexaura flexuosa* (cp23S-genotype B224). Because these variants are not commonly found in adult *Briareum* sp., they served as markers for uptake of exogenous *Symbiodinium*. The markers B211 and B223 cp23S-genotypes were not detected in any of 255 *Briareum* sp. colonies collected from the field; one colony harbored *Symbiodinium* B224 (21); 254 colonies harbored either *Symbiodinium* B178 and/or B184, the cp23S-genotypes typically found in *Briareum* sp. (21). The cp23S-genotypes used as markers in the experiment were not found in *Symbiodinium* isolated from the experimental colonies before or immediately after bleaching (Fig. 1 and Fig. 2A, lanes P and B; table S1).

Cell counts of *Symbiodinium* within *Briareum* colonies immediately after bleaching confirmed a decrease in symbiont density to less than 1% of the original population density (Fig. 2B). Molecular analysis detected residual populations of B178 and/or B184 in 27 of the 39 colonies after bleaching (table S1). During the subsequent 6-week exposure to exogenous symbionts, cell densities within the hosts increased 9- to 31-fold, demonstrating that the symbiosis had begun to reestablish itself (Fig. 2B). Molecular analysis of the symbiont population within these hosts after 3 and 6 weeks of exposure to exogenous *Symbiodinium* cultures identified the marker cp23S-genotypes in 58% and 45% of the samples, respectively (Fig. 2A, lanes R). This demonstrates repopulation of adult *Briareum* by exogenous symbionts and thus establishes a potential exogenous source of symbionts following bleaching events (22). Furthermore, 37% of the colonies that initially harbored *Symbiodinium* B178 and/or B184 contained only *Symbiodinium* with the marker cp23S-genotypes when sampled after 3 weeks of exposure to the exogenous algal source ["switching" sensu (11)]. In contrast, six colonies, which initially contained *Symbiodinium* B178 and/or B184, did not acquire symbionts with the marker cp23S-genotype. This may be due to physiological differences between the different *Symbiodinium* strains

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