

# Production of sulphate-rich vapour during the Chicxulub impact and implications for ocean acidification

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**The mass extinction event at the Cretaceous/Palaeogene boundary 65.5 Myr ago has been widely attributed to the Chicxulub impact<sup>1,2</sup>, but the mechanisms of extinction remain debated<sup>1,3-6</sup>. In the oceans, near-surface planktonic foraminifera suffered severe declines, in contrast to the relatively high survival rates of bottom-dwelling benthic foraminifera<sup>7</sup>. The vapour produced by an impact into Chicxulub's target rocks, which include sulphate-rich anhydrite, could have led to global acid rain, which can explain the pattern of oceanic extinctions<sup>4,5</sup>. However, it has been suggested that most of the sulphur in the target rocks would have been released as sulphur dioxide and would have stayed in the stratosphere for a long time<sup>6</sup>. Here we show, from impact experiments into anhydrite at velocities exceeding 10 km s<sup>-1</sup>, that sulphur trioxide dominates over sulphur dioxide in the resulting vapour cloud. Our experiments suggest that the Chicxulub impact released a huge quantity of sulphur trioxide into the atmosphere, where it would have rapidly combined with water vapour to form sulphuric acid aerosol particles. We also find, using a theoretical model of aerosol coagulation following the Chicxulub impact, that larger silicate particles ejected during the impact efficiently scavenge sulphuric acid aerosol particles and deliver the sulphuric acid to the surface within a few days. The rapid surface deposition of sulphuric acid would cause severe ocean acidification and account for preferential extinction of planktonic over benthic foraminifera.**

Global acid rainfall has been proposed as a mechanism leading to the demise of organisms at the Cretaceous/Palaeogene (K/Pg) boundary<sup>4,5</sup>, an interpretation that is based on the extensive distribution of sulphate-rich sediments in the vicinity of the impact site<sup>7</sup> and theoretical calculations related to the formation of shock-induced nitrogen oxide. If the hypothesized global acid rainfall was sufficiently intense to produce a marked reduction in the pH of ocean waters, this mechanism could have caused the worldwide extinction pattern of marine plankton<sup>6</sup>, the extinction of species on land and in fresh water<sup>8</sup>, and the subsequent fern spike<sup>9</sup>. However, important problems regarding the occurrence of such intense global scale acid rainfall immediately after the K/Pg impact are related to uncertainties in the molecular composition of sulphur

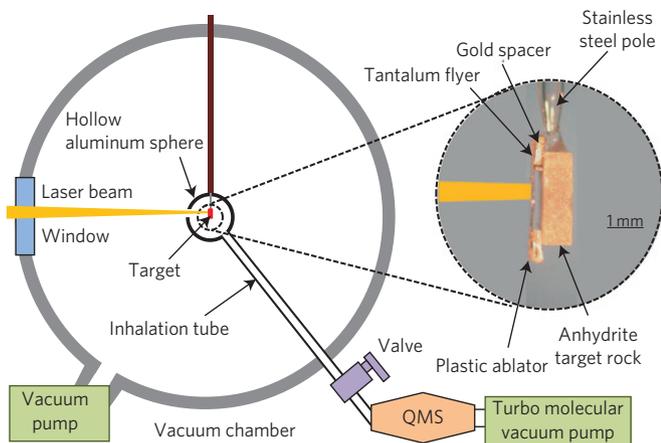
oxide gases released at the impact site. Specifically, the SO<sub>3</sub>/SO<sub>2</sub> ratios in the impact vapour cloud, which strongly influence the formation rates of sulphuric acid aerosols in the stratosphere (that is, the stratospheric conversion rates of SO<sub>3</sub> and SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>) are poorly constrained<sup>4,6,10</sup>. Notably, no previous impact experiments have investigated the chemical composition of impact-generated sulphate-rich vapour clouds, on account of the difficulties of accelerating macroscopic flyers (larger than submillimetre-sized, which are required to produce impact vapour volumes sufficient for quantitative measurements of vapour compositions) to velocities >10 km s<sup>-1</sup>, the conditions under which anhydrite (CaSO<sub>4</sub>) is vapourized.

As a substitute for impact vapourization, direct laser irradiation was used to analyse the chemistry of vapour plumes<sup>11</sup>; however, determination of K/Pg SO<sub>3</sub>/SO<sub>2</sub> ratios from the results of laser-irradiation experiments is difficult, as the pressure-temperature conditions of laser-induced vapour are different from those of impact-induced vapour. This problem has been overcome by the recent development of direct impact-induced gas analysis using a system in which flyers are accelerated using laser energy<sup>12</sup>, combined with quadrupole mass spectrometer (QMS) analysis<sup>13</sup>. Furthermore, a high-power laser with an energy of several kilojoules is available for laser guns, thus allowing thin-sheet and spherical flyers to be accelerated to velocities of much greater than 10 km s<sup>-1</sup> (refs 12,14). Thus, the combined use of a high-power laser gun and a QMS measurement system enables direct measurement of the molecular composition of impact-induced sulphur oxide gases and hence determination of the SO<sub>3</sub>/SO<sub>2</sub> ratio<sup>15</sup>.

Figure 1 presents a schematic of the experimental set-up. Tantalum foil flyers (thickness, 30 μm) were accelerated to velocities of 13–25 km s<sup>-1</sup> using a high-speed laser gun with a GXII-HIPER laser, housed at the Institute of Laser Engineering, Osaka University, Japan<sup>14</sup>. The plastic ablators (thickness, 50 μm) attached to the front surface of the tantalum foils were irradiated by the laser at a wavelength of 1,054 nm, a pulse width of 20 ns and an energy of 2–7 kJ. The laser energy was absorbed by the ablator and the ablation plasma accelerated the flyers to velocities of greater than 13 km s<sup>-1</sup>. Gold spacers (thickness, 200 μm) were placed between the flyers and natural anhydrite (CaSO<sub>4</sub>) target rocks. Peak shock pressures were estimated to be greater than 600 GPa, based

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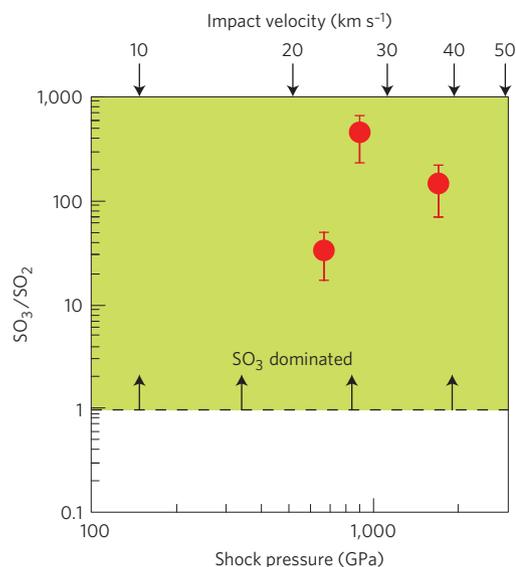
**Figure 1 | Schematic diagram of the experimental set-up.** A tantalum flyer and anhydrite target were placed in a large vacuum chamber. A laser-irradiated plastic ablator was attached to the front surface of the Ta flyer. The laser energy was absorbed by the ablator and the generated ablation plasma acted to accelerate the flyer. The chemical composition of the impact-induced vapour plume was measured directly using a quadrupole mass spectrometer (QMS). The vapour was introduced to the QMS using an inhalation tube. A hollow aluminium sphere was used to prevent the dispersal of the impact-induced gas.

on the impedance matching method; these pressures are greater than the vapourization threshold of anhydrite<sup>16</sup>. The influences of vapourization, fragmentation and obliquity of the flyer are negligible<sup>14</sup>. The flyers and targets were placed in a large vacuum chamber ( $<10^{-3}$  mbar) and the chemical compositions of the impact-induced vapour plumes were analysed directly by a QMS. The impact-induced S-bearing gas was introduced to the QMS using a stainless steel inhalation tube. A hollow aluminium sphere was used to minimize dispersion of impact-induced S-bearing gas to the large vacuum chamber and to improve the S/N ratio for the QMS analysis. Details of the experimental method are provided elsewhere<sup>15</sup>.

For each shot, we investigated the signal currents of mass numbers 48, 64 and 80, which correspond to the signals for SO, SO<sub>2</sub> and SO<sub>3</sub> (we confirmed the mass number—sulphur oxide correspondence from the isotopic ratios of terrestrial sulphur and oxygen<sup>15</sup>; also see Supplementary Information 1) and obtained the amounts of SO<sub>2</sub> and SO<sub>3</sub> released by the impacts. Figure 2 shows measured SO<sub>3</sub>/SO<sub>2</sub> ratios as a function of shock pressure. The upper horizontal axis in Fig. 2 indicates the impact velocity correspondence between anhydrite and Murchison meteorite, which is a candidate for the K/Pg impact body<sup>17</sup>. We used the planar impact approximation using Hugoniot of Murchison meteorite<sup>18</sup> and anhydrite<sup>16</sup>. Our experiment covers the expected range of impact velocities attributed to the K/Pg impact<sup>19</sup>.

The SO<sub>3</sub>/SO<sub>2</sub> ratios obtained here were of the order of 100 in every impact experiment, indicating that SO<sub>3</sub> is the dominant sulphur oxide species in impact vapour under the conditions of the experiments. As both theoretical calculations<sup>11</sup> and experiments indicate that larger scale vapour clouds yield higher SO<sub>3</sub>/SO<sub>2</sub> ratios, the SO<sub>3</sub>-rich composition on laboratory scales implies that the sulphur oxides generated by natural planetary-scale impacts are even more enriched in SO<sub>3</sub> relative to SO<sub>2</sub>. A detailed discussion of size-scaling issues is presented in Supplementary Information 2. Thus, SO<sub>3</sub> is expected to be the main sulphide component in the sulphur oxide gas released during the K/Pg impact.

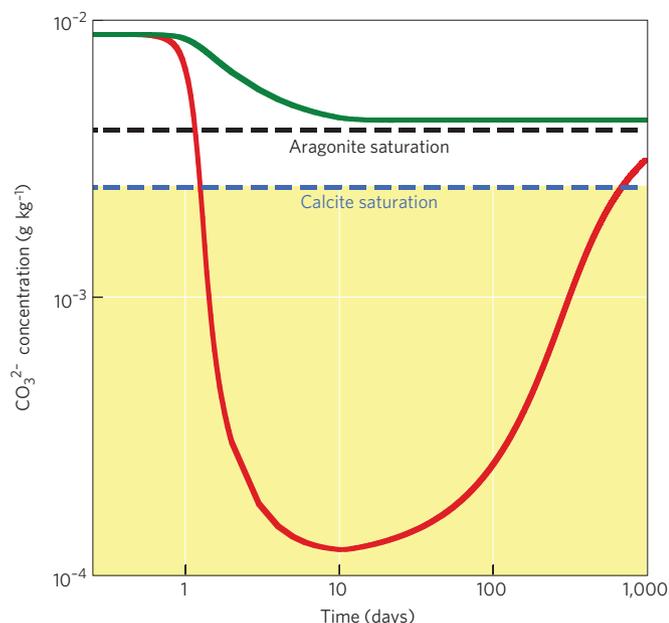
Next, we carried out theoretical calculations to explore the geological consequences of the release of huge amounts of SO<sub>3</sub> during the K/Pg impact (Supplementary Information 3). As well



**Figure 2 | The SO<sub>3</sub>/SO<sub>2</sub> ratios of impact-induced vapours as a function of impact velocities and peak shock pressures for impacts involving Murchison meteorite and anhydrite, obtained from the mass spectra of vapours using a QMS.** The data show that SO<sub>3</sub> is the dominant sulphur oxide species in the impact vapours at impact velocities of a few tens of kilometres per second. The error bars are related to the sensitivity error of the QMS. Variance between the experiments is related to the adhesion of SO<sub>x</sub> gases to the wall of the vacuum system.

as sulphates, the K/Pg impact generated large volumes of silicate particles; theoretical and field studies<sup>20,21</sup> have estimated that the mass of silicate particles ejected during the impact ( $\sim 10^{16}$  kg) was greater than that of sulphuric acid aerosols<sup>22</sup> ( $\sim 10^{14}$  kg). The silicate particles would have been ejected to space by the impact, although as much as half of the total mass of the ejected particles would have returned to the atmosphere within several hours of the impact, and a large mass of silicate particles would have continued to fall back to Earth even after  $\sim 10$  h or longer, depending on their ballistic orbits. By this time, most SO<sub>3</sub> gas would have settled to Earth where it would have rapidly combined with H<sub>2</sub>O in the atmosphere and condensed into sulphuric acid aerosol particles (Supplementary Information 3–1 and Supplementary Fig. 2). Most of the silicate particles were several tens to several hundreds of micrometres in diameter, as particles of this size make up most of the material within the K/Pg boundary layer at sites located at a distance from the Chicxulub crater<sup>23</sup>. Large silicate particles (diameters,  $\sim 100$   $\mu$ m) in the atmosphere settle much more quickly than sulphuric acid aerosol particles (diameters,  $\sim 1$   $\mu$ m; ref. 24) on account of their relatively high terminal falling velocities. As they fell, silicate condensate particles would have scavenged sulphuric acid aerosol particles in their path, efficiently removing the acid aerosol particles from the atmosphere. Thus, by the scavenging or sweeping out of acid aerosols by coexisting silicate particles, sulphuric acid would have settled to the ground surface within a very short time;  $\sim 50\%$  of the total mass load would have settled to the ground within one day, and approximately 70% of the total mass load would have settled to the ground within two days (the sweep-out model is described in detail in Supplementary Information 3–2; the result of a parametric study to assess the sensitivity of the results to the values of the parameters is shown in Supplementary Information 3–3).

Previous theoretical studies<sup>4,5</sup> of K/Pg sulphuric acid deposition assumed very slow rates of deposition of sulphuric acid aerosols (over periods of several months) and a small resultant reduction in oceanic pH (ref. 6; Supplementary Information 3–4). However,



**Figure 3 | Modelled temporal trends in the oceanic  $\text{CO}_3^{2-}$  concentrations at a water depth of 60 m, following the impact.** The red curve shows  $\text{CO}_3^{2-}$  concentrations calculated using the mass flux of sulphuric acid on the surface of the ocean. The green curve shows the  $\text{CO}_3^{2-}$  concentrations in the case of dissolution equilibria processes between  $\text{CO}_2$  in the oceans and atmosphere. The dashed lines indicate the saturation levels of aragonite and calcite. The yellow shading indicates undersaturation of the ocean with respect to  $\text{CaCO}_3$ .

our results, which show the  $\text{SO}_3$ -dominant composition of impact vapour, indicate that the timescale of sulphuric acid deposition would have been much shorter (two to three days) than that controlled by gas exchange equilibration between the atmosphere and the oceanic surface layer (approximately one year), as calculated from the modern atmosphere–ocean  $\text{CO}_2$  flux or from the globally averaged  $\text{CO}_2$  exchange coefficient. Thus, given such short timescales of  $\text{SO}_3$  deposition, the carbonate buffer in the marine surface layer would have been insufficient to modulate pH and  $\text{CO}_3^{2-}$  levels, resulting in significant decreases in both pH and  $\text{CO}_3^{2-}$  in most of the global marine surface layer. Figure 3 shows temporal trends in  $\text{CO}_3^{2-}$  concentrations in the oceanic surface layer based on such extremely short timescales of sulphuric acid fallout, taking into account vertical mixing in the ocean and ocean–atmosphere  $\text{CO}_2$  exchange (the calculation method is described in Supplementary Information 3–5). The results indicate that rapid surface deposition of sulphuric acid would have produced a dramatic global decrease in  $\text{CO}_3^{2-}$  concentrations and pH in the oceanic surface layer. The estimated minimum  $\text{CO}_3^{2-}$  concentrations are less than 10% of the saturation levels of carbonates, and the subsaturation levels of  $\text{CO}_2$  concentrations would have persisted for several years until ocean–atmosphere gas exchange had restored the carbonate buffer equilibrium.

The extremely intense acid rainfall and dramatic acidification of global marine surface waters can explain many of the features of the geologic record at the K/Pg boundary. For example, a previous study<sup>25</sup> showed that transient episodes of surface ocean acidification may have been the main cause of the extinction of calcifying plankton and ammonites. Such strong ocean acidification could account for the high rates of extinction of carbonate-secreting plankton species, which exceeded the extinction rates of silicate- and organic-secreting plankton<sup>26</sup>. Furthermore, strong acid rainfall and dramatic ocean acidification explain the high

rates of extinction of terrestrial and marine planktonic organisms, compared with the moderate rates of extinction observed in freshwater organisms, as acidification of freshwater environments would have been relatively less intense on account of the acid-neutralizing effects of larnite ( $\beta\text{-Ca}_2\text{Si}_2\text{O}_4$ ) generated by the impact<sup>8</sup>. Moreover, the occurrence of rapid global acidification is consistent with an increase in the abundance of ground ferns (the so-called fern spike), which are tolerant to acidic water-logged conditions, at the K/Pg boundary<sup>9</sup>. Intense acid rainfall would also have resulted in enhanced weathering of continental crust and the resulting increase of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, as observed at the K/Pg boundary<sup>27</sup>. Both Sr and Li isotopes indicate enhanced continental weathering following the K/Pg impact<sup>28</sup>, although some studies have reported that Cenozoic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are decoupled from silicate weathering rates<sup>29</sup>. Furthermore, the etched crystal surfaces of K/Pg spinels found in Bulgaria may be the result of high stratospheric densities of sulphuric acid aerosols after the impact<sup>30</sup>. These lines of evidence strongly suggest that concentrated sulphuric acid rains and intense ocean acidification by  $\text{SO}_3$ -rich impact vapours resulted in severe damage to the global ecosystem and were probably responsible for the extinction of many species after the K/Pg event. Finally, it is noteworthy that, although  $\text{SO}_3$ -rich vapour may be responsible for the K/Pg mass extinction,  $\text{SO}_3$ -rich rocks are not necessarily found at impact sites other than Chicxulub. This suggests that the target lithology could control the severity of impact-related mass extinction events.

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### Author contributions

S.O., T.K., T.M. and S.S. conceived the study and wrote the paper. S.O., T.K., K.K., T.H., T. Sakaiya, K.S., Y.H., T. Sano, T.W., K.O. and S.S. carried out the experimental work using the GXII and analysed the results. S.O. and S.S. created the sweeping out model and carried out the calculations.

### Additional information

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### Competing financial interests

The authors declare no competing financial interests.