

HIGH TEMPERATURE VAPORIZATION OF QUARTZ-CALCITE-ANHYDRITE/GYPSUM TARGETS IN RELATION TO CHICXULUB IMPACT. M.V. Gerasimov, Space Research Institute, RAS Moscow, Yu.P. Dikov, Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry, RAS Moscow, O.I. Yakovlev, Vernadsky Institute of Geochem. and Analytical Chemistry, RAS Moscow, Russia; and F. Wlotzka, Max-Planck-Institut für Chemie, Abteilung Kosmochemie, Mainz, Germany.

Chicxulub crater is considered to be formed by the possible impact event which resulted in K/T mass extinction [1,2]. The presence of thick deposits of anhydrite in the target rocks must have resulted in the liberation of enormous quantities of sulfur gases and the synthesis of noticeable quantities of sulfur acid aerosols which could strongly affect the biosphere [3]. During a previous set of experiments [6] we investigated the vaporization of pure anhydrite and gypsum and found that a large quantity of the evolved sulfur is efficiently trapped in the forming condensate. Here we have investigated the high temperature vaporization of mixtures of quartz, calcite and gypsum or anhydrite. This experiment showed that isolated and chain calcium silicates are formed in the resulting condensate. More sulfur remains in the atmosphere in the presence of silicon in the target, since a certain amount of calcium is bound as calcium silicates and less calcium is available for the formation of sulfates in the condensate.

A possible vital role of sulfur during Chicxulub impact encouraged us to investigate the influence of various factors on the efficiency of SO_2 and SO_3 liberation during high-temperature impact vaporization. The strategy was to include carbonates and silicates in the experiment because: 1) The upper parts of the target rocks represent layered structures of carbonates and sulfates [4], and vaporization of anhydrite and carbonates proceeded together; 2) A sufficient part of vaporized material must come from silicates from the crystalline basement.

In this set of experiments we have prepared samples from mixtures which could qualitatively simulate the real target. As an additive of carbonate we used calcite and to simulate silicates we used quartz. In one set of experiments we used anhydrite (CaSO_4) and in another gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to simulate the possible role of water from the oceanic shelf. Mixtures were prepared with the following ratios: 1) CaSO_4 : CaCO_3 : $\text{SiO}_2 = 1:1:2$ and 2) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: CaCO_3 : $\text{SiO}_2 = 1:1:2$ (mole ratio). High temperature vaporization was provided using a powerful neodymium glass pulse laser [5,6]. Samples were vaporized in a cell filled with air at 1 atm. at room temperature. The condensate was collected on a Ni foil placed in the path of the spreading vapor cloud at a distance of 6 cm. The condensed film was analysed using X-ray photoelectron spectroscopy (XPS). The film was etched layer by layer (with a step ranging from 100 to 400 Å) by argon ions and for every step XPS analyses were performed providing a cross-section of the film. XPS analyses provided both information on elemental composition and on charging state of the elements.

Chemical composition of condensed films from both samples are presented in Tables 1 and 2. A certain depletion in volatiles (sulfur, carbon) is evident in the condensate, it contains no water. While rock forming elements are almost totally condensing back from a vapor the volatiles can remain in gaseous form, but some of them can be trapped in the condensate by reactions with rock forming elements. If we assume that all evaporated calcium is condensed then the ratio of calcium to volatiles will indicate the degree of the disproportionation between gaseous and trapped forms. Target samples had Ca:S:C ratio = 1:0.5:0.5 and for condensate from mixture 1 the ratio is Ca:S:C=1:0.2:0.3 and from mixture 2 - Ca:S:C=1:0.2:0.2. About 40% of sulfur and from 40% to 60% of carbon is trapped from the vapor cloud to the condensate. As in our previous experiments [6] the main phase of sulfur in the condensate is CaSO_4 . Carbon is present as carbonate and in the condensate from mixture 1 about 45% of carbon is free carbon. As a consequence, we can estimate that all the water, about 60% of sulfur and about 50% of carbon remain in gaseous form in the atmosphere. In comparison with our previous experiments on vaporization of gypsum and anhydrite without the addition of silicate [6], we have more sulfur and carbon which remained in the gaseous phase. Thus in case of pure anhydrite only 17% of sulfur was not trapped by forming a condensate [6]. In case of gypsum the efficiency of trapping was less indicating the possible role of water. The presence of silicon in a sample provides more efficient volatilization of sulfur since a part of calcium is bound with silicon to produce calcium silicates.

Silicon in the condensate almost totally lost its initial structure. Only in case of the gypsum containing sample mixture 2 a small amount of silicon (~12%) is present in the condensates in framework structure as in the original quartz target, most of it is present in isolated and chain structures. The ratio of chain to isolated structures is about 1 : 1 for the condensate from sample 1 and 1.6 : 1 from sample 2. Analyses of the structural state of silicon in condensates shows that we have mineral embryos of wollastonite and larnite groups. It can be an interesting outcome for Chicxulub impact that vaporization of its anhydrite-calcite-silicate target could result in production by condensation of large quantities of dispersed stable calcium silicates. Probable is the production of a full range of calcium silicates. The presence of such volatiles as water, sulfur and carbon in the vapor cloud makes possible the

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formation of such rare minerals as ellestadite $\text{Ca}_5[\text{OH}(\text{SiO}_4, \text{SO}_4)]$, spurrite $\text{Ca}_3[\text{CO}_3(\text{SiO}_4)_2]$, thaumasite $\text{Ca}_3\text{H}_2[\text{CO}_3|\text{SO}_4|\text{SiO}_4]*13\text{H}_2\text{O}$ (and others) in the condensate.

The condensates from sample mixtures 1 and 2 differ noticeably in oxidation state of sulfur and carbon. During vaporization of water-free sample mixture 1 thermo-reduction took place. A certain amount of reduced phases were measured: 0.6 at% of S^{-2} , 2.1 at% of C^0 , 0.02 at% of CO , 0.2 at% of Si^0 . The presence of nearly half the carbon in reduced form correlates with the finding of free carbon in K/T boundary layers, which are ascribed to global wood fire, however. The absence of reduced phases (S^{-2} , Si^0 , C^0) in the condensate from water-containing sample mixture 2 indicates the oxidative role of water. All carbon is bound in carbonates. It can be expected that the presence of water in the vapor cloud will result in higher production of CO_2 and SO_3 .

Our experiments with vaporization of sulfate-carbonate-silicate targets leads to the following conclusions:

1) The efficiency of volatilization of sulfur to the atmosphere is higher in the presence of silicon since a certain amount of calcium is bound to calcium silicates. 2) Vaporization of silicate-carbonate-sulfate targets result in the formation of mainly isolated and chain calcium silicates which can be indicative of vapor condensation origin of fireball ejecta. 3) The presence of water in the vapor cloud increases the oxidation state of condensation products and probably provides higher production of CO_2 and SO_3 .

References: [1] Pope K.O. et al. (1991) *Nature* 351, 105; [2] Hildebrand A.R. et al. (1991) *Geology* 19, 867; [3] Brett R. (1992) *LPSC XXIII*, 157; [4] Pope K.O., Ocampo A.C. (1992) *LPSC XXIII*, 1097; [5] Gerasimov M.V. et al. (1985), *Vestnik Akad. Nauk USSR* 9, 10 (in Russian); [6] Gerasimov M.V. et al. (1994) *LPSC XXV*, 413.

Table 1. Composition (at%) of different layers in condensed films from mixture 1, $\text{CaSO}_4+\text{CaCO}_3+\text{SiO}_2$

Elements Chemical state	Ca	Si ⁰	Si isol.	Si chain	S ⁻²	S S ⁺⁴	S ⁺⁶	C ⁰	C C ⁺²	C ⁺⁴	O
Surface-100 Å	12.2	-	2.4	11.3	0.1	2.9	5.6	0.9	0.3	0.5	64.0
100-200 Å	16.0	-	5.4	10.2	0.3	1.5	2.8	1.2	-	1.5	61.1
200-400 Å	17.1	-	6.6	8.6	0.5	1.1	2.0	2.0	-	2.4	59.7
400-600 Å	16.3	-	7.1	8.2	0.6	1.0	1.6	2.6	-	2.8	59.6
600-800 Å	17.3	-	8.4	6.5	0.6	0.9	1.5	2.2	-	3.0	59.6
800-1200 Å	17.4	-	8.9	5.8	0.6	0.8	1.6	2.2	-	3.1	59.6
1200-1600 Å	17.8	1.0	7.9	6.8	0.7	0.8	1.4	2.4	-	2.8	58.6
Average	16.9	0.2	7.4	7.4	0.6	1.1	1.9	2.1	-	2.6	59.7
	16.9		15.0			3.6		4.7			59.7

Table 2. Composition (at%) of different layers in condensed films from mixture 2, $\text{CaSO}_4*2\text{H}_2\text{O}+\text{CaCO}_3+\text{SiO}_2$

Elements Chemical state	Ca	Si isol.	Si chain	Si frmw.	S S ⁺⁴	S S ⁺⁶	C (CO_3) ⁻²	O
Surface- 100 Å	14.3	3.6	7.8	1.2	1.4	5.8	2.1	63.8
100 - 300 Å	15.6	4.2	7.7	2.0	1.0	2.8	4.4	62.4
300 - 500 Å	17.4	4.7	7.7	1.5	0.9	2.0	4.2	61.6
500 - 700 Å	19.6	5.4	7.2	1.8	0.8	1.8	2.8	60.6
Average	17.1	4.6	7.6	1.7	1.0	2.7	3.5	61.8
	17.1		13.9		3.7		3.5	61.8