

**ANHYDRITE EOS AND PHASE DIAGRAM IN RELATION TO SHOCK DECOMPOSITION.** B. A. Ivanov<sup>1</sup>, F. Langenhorst<sup>2</sup>, A. Deutsch<sup>3</sup>, and U. Hornemann<sup>4</sup>, <sup>1</sup>Institute for Dynamics of Geospheres, Russian Acad. Sci., Leninsky Prospect 38/6, Moscow, Russia 117939, (baivanov@idg.chph.ras.ru), <sup>2</sup>Bayerisches Geoinstitut (BGI), Univ. Bayreuth, D-95440 Bayreuth, Germany, (falko.langenhorst@uni-bayreuth.de); <sup>3</sup>Inst. f. Planetologie (IfP), Univ. Münster, D-48149 Münster, Germany, (deutschca@uni-muenster.de); <sup>4</sup>Ernst-Mach-Institut (EMI), Am Klingelberg 1, D-79588 Efringen-Kirchen, Germany (hornema@wiwei.emi.fhg.de)

**Introduction:** In the context of the Chicxulub impact, it became recently obvious that experimental and theoretical research on the shock behavior of sulfates is essential for an assessment of the role of shock-released gases in the K/T mass extinction. The Chicxulub crater is the most important large impact structure where the bolide penetrated a sedimentary layer with large amounts of interbedded anhydrite (Haughton has also significant anhydrite in the target). The sulfuric gas production by shock compression/decompression of anhydrite is an important issue, even if the size of Chicxulub crater is only half of the so far assumed size [1].

The comparison of experimental data for anhydrite, shocked with different techniques at various laboratories, reveals large differences in the threshold pressures for melting and decomposition (e.g. [2, 3]). To gain insight into this issue, we have made a theoretical investigation of the thermodynamic properties of anhydrite. The project includes the review of data published in the last 40 years - reasons to study anhydrite cover a wide field of interests: from industrial problems of cement and ceramic production (e.g. [4]) to the analysis of nuclear underground explosions in salt domes, conducted in the USA and USSR in the 1970<sup>th</sup> (e.g. [5-7]).

**Review of available data:** According to these data anhydrite is as a material with a complex behavior in various aspects. Static and shock compression shows that anhydrite has two solid-solid polymorph phase transitions at high pressure. At least the second one is a martensitic transformation, which causes a double shock wave structure in the relevant pressure range. Annealing experiments at high temperature and normal pressure reveal a complex behavior near to the melting point ( $T \sim 1738$  K). The melting point of anhydrite is very close to the temperature of the decomposition reaction  $\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2$ . In case of a closed system, anhydrite may melt congruently, i.e., the partial  $\text{SO}_2$  pressure suppresses the decomposition. However, in an open system from which  $\text{SO}_2$  is removed, anhydrite melts incongruently. In the latter case, the eutectic melting of mixture with 75%  $\text{CaSO}_4$  and 25%  $\text{CaO}$  (75%+25%) may occur at  $T \sim 1638$  K. The kinetics of the decomposition reaction is very

slow; degassing of a 0.5 g sample takes several hours [1].

**Equation of state:** To reconcile known experimental data, we made an attempt to construct the phase diagram and equation of state of anhydrite, which can then be used to numerically model shock experiments and natural impact events.

*Equilibrium phase diagram* (Fig. 1). The p-T phase diagram is compiled with a standard set of thermodynamic data for  $\text{CaSO}_4$ ,  $\text{CaO}$ ,  $\text{SO}_2$ , and  $\text{O}_2$ . A simple Fortran program allows us to vary the partial pressures for  $\text{SO}_2$  and  $\text{O}_2$  gases resulting in p-T curves for the decomposition of anhydrite under various  $\text{SO}_2$  venting conditions.

*ANEOS trial tables* (Figs. 2, 3). To model the pressures and temperatures of anhydrite under shock compression and decompression, we used the modified Fortran code ANEOS (ANalytical Equation Of State, Los Alamos design), which allowed us to construct separate fields for three solid phases of  $\text{CaSO}_4$ . As ANEOS computes all thermodynamic properties for a material, we can estimate also phase boundaries. Due to the lack of high-pressure compressibility data for anhydrite, we made the ANEOS construction for the quartz-coesite-stishovite system (Fig. 2) and assumed a similar general phase boundary geometry for 3 phases of  $\text{CaSO}_4$ . This provided first hints to the geometry of phase boundaries in the  $\text{CaSO}_4$  system. Fig. 3 shows multi-phase ANEOS estimates for the Hugoniot (shock front) and release temperatures. At pure hydrostatic conditions, anhydrite may melt when released from pressures between 80 to 90 GPa. Under real conditions, plastic work due to shear strain can readily dissipate additional heat in the sample and reduce the onset pressure for melting and degassing.

**Preliminary conclusions:** The presented ANEOS-based equation of state for anhydrite provides the basis for refined computer modeling of natural impact events and laboratory experiments. The model-derived values of shock pressure for impact melting and impact decomposition are in the same range of values as in previous estimates [8, 9]: for non-porous anhydrite we predict melting in the pressure range of 80 to 90 GPa, and incipient decomposition at pressures from 60 to 70 GPa for venting of gas products, and from 100 to 110 GPa for gas products of the reaction in equilib-

rium. The slow kinetic of decomposition near to the melting point requires sophisticated numerical modeling for more reliable estimates of sulfur gases production due to impact events.

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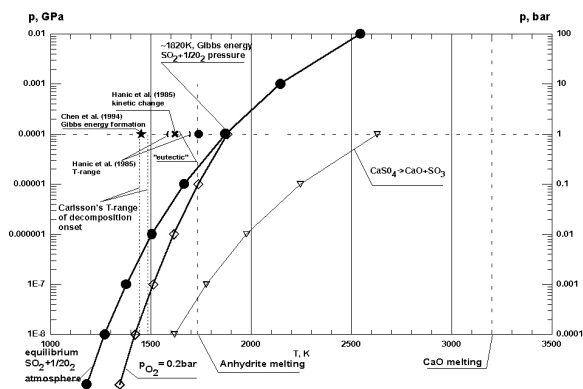


Fig. 1. p-T diagram for the decomposition of anhydrite under an equilibrium atmosphere of sulfur dioxide and oxygen and an atmosphere with 0.2 bar oxygen and variable pressure of SO<sub>2</sub>. Decomposition equilibrium estimates for CaSO<sub>4</sub> → CaO + SO<sub>3</sub> reaction is shown for comparison.

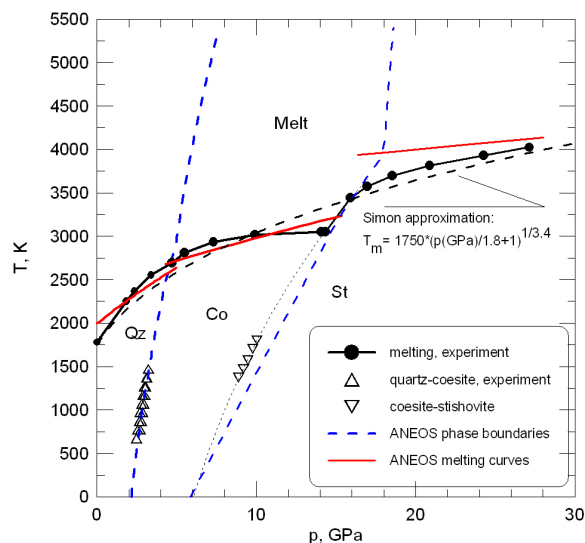


Fig. 2. The ANEOS three-phase model of quartz with coesite and stishovite in equilibrium at phase boundaries (blue dashed curves). Experimental data for melting and phase equilibrium are shown for comparison. A simple Simon approximation may be used in the numerical modeling to estimate quartz melting in computations without an explicit presentation of phase transitions.

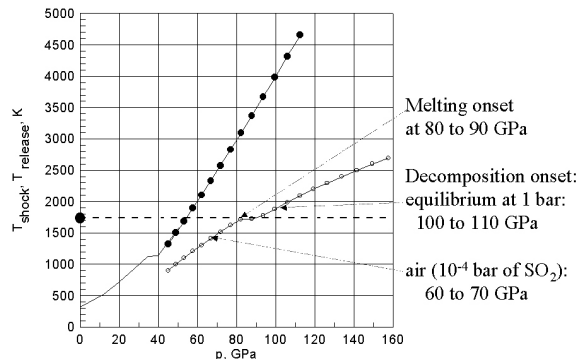


Fig. 3. Hugoniot and released temperatures estimated for anhydrite by the ANEOS code. In dependence of the SO<sub>2</sub> partial pressure, the decomposition may start below or above the melting point.