



# Experimental constraints on the destabilization of basalt + calcite + anhydrite at high pressure–high temperature and implications for meteoroid impact modeling

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## ABSTRACT

Calcite  $\text{CaCO}_3$  and anhydrite  $\text{CaSO}_4$  are two sedimentary components or alteration products of basalts on the Earth, Venus, and Mars. The fate of anhydrite-, calcite-bearing crust during a meteoroid impact must be addressed in order to evaluate: (1) the potential S- and C-gas release to the atmosphere, (2) the formation of S- and C-rich melts, and (3) the crystallization of S- and C-rich minerals which may be recognized by spectral analyses of planetary surfaces. We performed piston-cylinder experiments at 1 GPa, between 1200 and 1750 °C, on a mixture of 70 wt.% tholeiitic basalt + 15 wt.% anhydrite + 15 wt.% calcite. Up to ~1440 °C, an ultracalcic ( $\text{CaO} > 19.8$  wt.%;  $\text{CaO}/\text{Al}_2\text{O}_3 > 1$  wt.%) picrobasaltic ( $\text{SiO}_2$  ~39–43 wt.%;  $\text{Na}_2\text{O} + \text{K}_2\text{O} < 2$  wt.%) melt containing up to 5.7 wt.%  $\text{SO}_3$  and up to 5.1 wt.%  $\text{CO}_2 + \text{H}_2\text{O}$  (calculated by difference) is present in equilibrium with fassaitic clinopyroxene, anhydrite, scapolite, chromian spinel and a gas composed mainly of CO and, occasionally, aliphatic thiols like  $\text{CH}_3(\text{CH}_2)_3\text{SH}$ . Hydrogen was incorporated either by contact between the starting material and air or by diffusion through the capsule during the experiments. Above ~1440 °C, a CaO-rich (~35 wt.%) sulfate–carbonate (SC) melt which contains 41–47 wt.%  $\text{SO}_3$ , 7–12 wt.%  $\text{CO}_2 + \text{H}_2\text{O}$  and a few percent of  $\text{Na}_2\text{O}$ , forms in equilibrium with the picrobasaltic melt. This study shows that a meteoroid impact onto an anhydrite- and calcite-bearing basaltic crust is likely to release CO gas to the atmosphere, while S is trapped in solid or liquid phases. Under hydrous conditions, however, the S/C in the gas may increase. The importance of the temperature parameter on the impact phase relations is also demonstrated. In particular, SC melt may form by meteoroid impact, and flow rapidly on a planetary surface. Physical modeling must therefore be combined with high  $P$ -high  $T$  phase diagrams of complex assemblages similar to planetary lithologies in order to evaluate the effects of a meteoroid impact.

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## 1. Introduction

Calcite  $\text{CaCO}_3$  and anhydrite  $\text{CaSO}_4$  are two sedimentary components or alteration products of basalts in contact with either ocean or atmosphere on the Earth (Alt and Teagle, 1999; Plank and Langmuir, 1998; Spencer, 2000), Venus (Fegley et al., 1992; Kargel et al., 1994) and Mars (Bibring et al., 2007; King and McLennan, 2010; Squyres et al., 2004). The fate of anhydrite-, calcite-bearing crust during a meteoroid impact must be addressed in order to evaluate (1) the potential S and C gas release to the atmosphere, which may provoke important climate changes (Gupta et al., 2001, 2002), (2) the formation of S- and/or C-rich melts (Osinski et al., 2008), which may flow faster than silicate melts on planetary surfaces and (3) the crystallization of other S and C minerals like carbonates, graphite/diamond, sulfate, sulfide or scapolite which may be recognized by spectral analyses of planetary surfaces.

For example, the Chicxulub impact (~65.5 Myr ago) in Yucatan Peninsula (Mexico) is known to have produced gas and melts rich in carbon and sulfur (Deutsch and Langenhorst, 2007; Dresser et al., 2004; Hecht et al., 2004; Jones et al., 2000; Schulte et al., 2009), because the impact target was a carbonate and sulfate-rich sediment platform lying on a basaltic/andesitic crust (Giuli et al., 2008; Sigurdsson et al., 1991a, 1991b). This gas release is suspected to be the cause of the K–Pg extinction. No impact melt flow was recorded, probably because of the asteroid's size and of the presence of surface water, but carbonate and silicate melt drops formed, which can now be observed in various geologic horizons. Carbonate and silicate immiscible melts produced during impact events have been reported in Germany and Canada (Graup, 1999; Osinski and Spray, 2001). Impact-generated sulfate–carbonate melts were also evoked to explain the very long channels (canali) observed at Venus surface (Kargel et al., 1994; Treiman, 2007), although no link between these channels and impact craters was found.

A meteoroid impact on a planetary surface implies a sudden increase of pressure  $P$  and temperature  $T$  in a limited volume of material. These parameters evolve as a function not only of the size,

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density, temperature, trajectory and speed of the impactor (Collins et al., 2005), of the ground composition, but also of the radial distance from the point of impact (Ugalde et al., 2005) and of time. At the impact site, the very high  $P$  and  $T$  ( $>1700$  °C; Schultz et al., 2006) conditions are likely to cause partial or complete devolatilization of calcite and anhydrite, if these minerals appear alone. As the distance from the impact location increases,  $P$  and  $T$  rapidly decrease, leading to conditions where no mineralogical changes are expected. After the impact,  $P$  is rapidly released, much faster than  $T$ . Low  $P$ /high  $T$  conditions are readily achieved, which are favorable to melting and devolatilization. The whole  $P$ – $T$  field (not only the pressure peak) must therefore be considered to determine the consequences of an impact. Moreover, the devolatilization and melting processes are strongly dependent on the chemical system. Complex lithologies such as those appearing at planetary surfaces must therefore be studied.

Static high pressure (HP) experiments have been used in combination with physical calculations to study the fate of rocks during meteoroid impacts (Sharp and DeCarli, 2006; Sigurdsson et al., 1991a, 1991b). Experimental petrology methods and thermodynamic calculations allow one to constrain the potential evolution of a given material at any  $P$  and  $T$ . Some HP experimental or theoretical studies have been performed on basalt, anhydrite and calcite separately or on a combination of two (Fig. 1). HP melting of basalt has been investigated by numerous authors (e.g., Petermann and Hirschmann, 2003; Takahashi et al., 1998). At 1 GPa, the liquidus temperature of a tholeiitic basalt is  $\sim 1270$ – $1300$  °C (Villiger et al., 2004). The crystallization order is olivine, spinel, clinopyroxene, orthopyroxene, and plagioclase. At ambient pressure, anhydrite decomposes at  $\sim 1325$  °C, and at 10 GPa at  $\sim 1500$  °C (Fig. 1; Yang and Ahrens, 1998). Calcite melts at  $\sim 1400$  °C at 1 GPa, and  $\sim 1700$  °C at 6 GPa (Ivanov and Deutsch, 2002; Suito et al., 2001). Devolatilization of calcite was observed at 17–18 GPa (Boslough et al., 1982), but may start below 10 GPa (Lange and Ahrens, 1986). Eutectic melting of a calcite + anhydrite mixture occurs at 977 °C at 100 bars (Fuerstenau et al., 1981; Treiman, 1995). HP melting of “basalt” + calcite has been studied by several authors, using either a model eclogite composition (Yaxley and Brey, 2004; Yaxley and Green, 1994) or an altered basalt

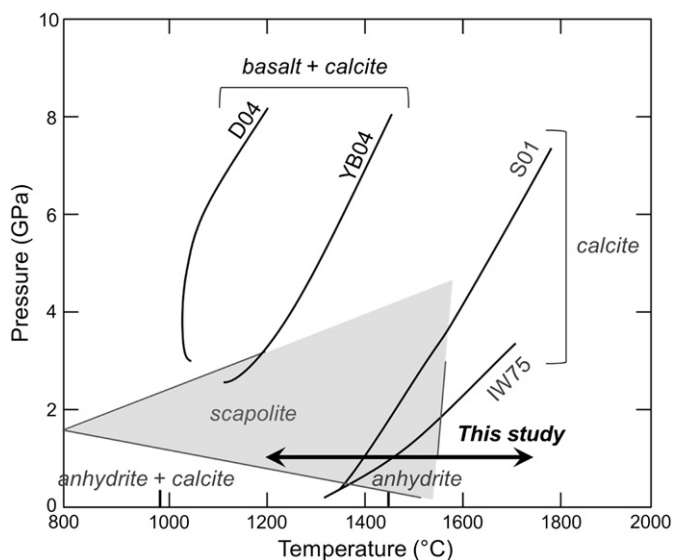


Fig. 1. Pressure–temperature diagram showing the solidus location for calcite, anhydrite, calcite + anhydrite and basalt + calcite systems determined by different authors either by experiments or by calculations. S01: Suito et al. (2001). IW75: Irving and Wyllie (1975). Anhydrite + calcite is from Treiman (1995). YB04: Yaxley and Brey (2004). D04: Dasgupta et al. (2004). S–C–scapolite stability field is from Papike et al. (2007).

containing water (Dasgupta et al., 2004). They all observed that the high temperature (HT) interactions between basalt and calcite produce a carbonate-rich ionic melt. They also show that various solid carbonate phases (magnesite, dolomite, aragonite) appear at the solidus temperature depending on the pressure. In the basalt + anhydrite system, a sulfate melt is stable at 1 GPa– $1300$  °C and  $fO_2 \sim FMQ + 2$  (Jugo et al., 2005). In a hydrous basalt + S system at 0.4 GPa– $1100$  °C, anhydrite and sulfides form in equilibrium with a silicate melt (Pichavant et al., 2006). To our knowledge, the system basalt + calcite + anhydrite has never been experimentally or theoretically investigated.

In this study, we performed HP experiments using a mixture of 70 wt.% basalt + 15 wt.% calcite + 15 wt.% anhydrite. We focus on the role of  $P$  and  $T$  on the phase relations and redox interactions which determine the amount of gas/melt that might be released. Experiments were performed at 1 GPa because (1) the pressure imposed on the rocks is lower when the distance from the impact location increases and (2) pressure decreases much faster than temperature after an impact. This pressure was also chosen to compare the results with the existing data on the basalt (Villiger et al., 2004), calcite (Irving and Wyllie, 1975; Suito et al., 2001) and basalt + anhydrite (Jugo et al., 2005) systems. A large temperature range ( $1200$  °C to  $1750$  °C) was investigated in order to cover most of the solidus–liquidus field.

## 2. Experimental and analytical methods

### 2.1. Experimental method

#### 2.1.1. Starting material

A tholeiitic basalt composition was chosen to represent oceanic basalts, which cover  $\sim 70\%$  of the Earth's surface. Tholeiites are also probably present on Venus' surface, although there may be alkali-rich basalts as well. We used the synthetic tholeiitic basalt glass composition HK#19 (Hirose and Kushiro, 1993), which was studied by Villiger et al. (2004) at 1 GPa from 1060 to 1330 °C. A similar composition was prepared using a 2-step method. First, oxides and carbonates ( $CaCO_3$ ,  $Na_2CO_3$  and  $K_2CO_3$ ) were mixed and ground in an agate mortar under ethanol. This mixture was dried and melted under air to a decarbonated glass in a high temperature furnace. The recovered glass was crushed, and melted again twice. The resulting powder was mixed with a synthetic fayalite in proportions leading to HK#19. We then prepared a mixture of 70 wt.% glass, 15 wt.% calcite  $CaCO_3$  (Alfa Aesar) and 15 wt.% anhydrite  $CaSO_4$  (Alfa Aesar), with  $SiO_2 = 34.39$  wt.%,  $TiO_2 = 0.42$  wt.%,  $Al_2O_3 = 10.63$  wt.%,  $Cr_2O_3 = 0.25$  wt.%,  $FeO = 5.28$  wt.%,  $MnO = 0.10$  wt.%,  $MgO = 9.18$  wt.%,  $CaO = 23.15$  wt.%,  $Na_2O = 1.11$  wt.%,  $K_2O = 0.06$  wt.%,  $SO_3 = 8.85$  wt.%,  $CO_2 = 6.60$  wt.% (“BCA” composition).

#### 2.1.2. Experimental setting

Samples were loaded into 3 mm gold–palladium (for experiments up to  $1440$  °C) or platinum ( $1440$  °C to  $1750$  °C) capsules which were welded at each end using a tungsten–argon welder to minimize exchanges with the surrounding environment. Whole capsules, as well as polished sections were carefully checked by optical microscopy before and after experiments in order to verify the welding integrity. Experiments were performed at 1 GPa between  $1200$  and  $1750$  °C using a non-end-loaded piston–cylinder press (Quickpress®, 1/2”). Barium carbonate was used as pressure medium and a graphite tube as heater. Temperature of the sample was measured by a  $W_5Re_{95}$ – $W_{26}Re_{74}$  thermocouple (type C) just below the capsule. The experimental assembly is similar to the one used by Righter et al. (1997), except that a MgO sleeve was used between the capsule and the furnace. Temperature gradients are thought to be small (less than  $10$  °C) because of the small length of the capsules (1.5–2 mm).

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