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CO_2 Emission Accompanying the Fracture of Calcite

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Abstract. Time resolved mass spectroscopy of the emissions accompanying the fracture of calcite (rhombohedral $CaCO_3$) show that the principle volatile product, CO_2, is released in bursts milliseconds after the fracture event. Similar measurements during the abrasion of calcite and during low temperature thermal decomposition of pulverized calcite show similar CO_2 bursts. We argue that the observed bursts reflect localized decomposition of the calcite during the relaxation of reversible plastic deformation created by fracture and abrasion. This implies that mechanical, non-thermal processes play an important role in producing the observed decomposition products.

Introduction

The fracture of calcite (rhombohedral $CaCO_3$) is accompanied by the emission of CO_2, (Fox and Soria-Ruiz 1970; Upakaev 1990) the volatile product of calcite decomposition. Here we report time-resolved measurements of CO_2 emission due to fracture which indicate that emission typically begins some milliseconds *after* the completion of fracture. This is inconsistent with the commonly invoked thermal decomposition mechanism due to heat generated by crack growth. This mechanism would necessarily yield prompt emission. Previous work with alkali halides leads us to suggest that mechanical processes, i.e., relaxation of plastic deformation created during deformation and fracture, play a key role in the observed decomposition. An understanding of the decomposition process may yield insight into the coupling of mechanical energy to chemical and electronic processes associated with defect production and decomposition. The decomposition of calcite under meteoroid impact is relevant to some models of planetary evolution (Lange and Ahrens 1986).

Fracture-related emission of light as well as charged and neutral particles (collectively known as *fracto-emission*) have been observed in many minerals (Langford and Dickinson 1989). In particular, we have observed the emission of neutral atoms and molecules after fracture of single crystal MgO (Dickinson et al. 1986), alkali halides (Dickinson et al. 1991a), and germanium (Dickinson et al. 1991b). Recent evidence suggests that these delayed emissions are related to dislocations generated during crack growth (Dickinson et al. 1991a and b). Near-surface dislocations are unstable and are attracted toward the fracture surface by an image force. The energy released by the arrival of a dislocation at the surface can be sufficient for the ejection of thousands of neutral molecules. Similar processes could be responsible for the creation of "hot-spots" in deformed and fractured material (Armstrong et al. 1982; Yoo et al. 1984). Although room temperature deformation of calcite does not generally involve dislocation motion, a similar process (twinning) does allow for substantial plastic deformation (Kaga and Gilman 1969; Anuradha and Bhagavan Raju 1986) and may play a corresponding role in the emissions reported below.

Calcite decomposition occurs thermally at 900° C, and has been long regarded as the archetypical decomposition reaction (Thomas and Renshaw 1967; Searcy and Beruto 1976). The decomposition of calcium carbonate is a key step in the production of lime, a commercially important material in several industries. Its decomposition kinetics are significantly influenced by the previous thermal history and the presence of defects, most notably dislocations (Thomas and Renshaw 1967), but these influences are still not entirely understood. The decomposition of calcite accompanying fracture may yield insights into the solid state chemistry of the response of such minerals to mechanical stimulation (e.g., impact) as well as to thermal stimulation.

Experiment

Natural, optical grade calcite (variety Iceland spar from Mexico) was cut into $2 \times 6 \times 12$ mm^3 platelets. The samples were loaded into a sample carousel which was mounted in an ultrahigh vacuum

system with a base pressure of less than 1 μPa. After pumpdown, the samples were loaded to fracture in three point bend across a span of 6.3 mm. Neutral molecules leaving the sample were ionized by an electron impact ionizer (70 eV electron energy, 2 mA emission current) whose entrance was positioned 6 mm from the tensile face of the sample. The resulting ions were mass filtered with a UTI 100C quadrupole mass spectrometer. Output from the detector (a Channeltron electron multiplier) was fed into a fast electrometer (time constant ~25 μs) and the resulting voltage signal digitized at 10 μs intervals. Simultaneous load measurements were made with a quartz load transducer mounted behind the loading nose. Tests of the system indicate that the time of fracture can be reliably determined to within 10 μs from the onset of the drop in the load signal, subtracting the measured time delay for the stress change to reach the transducer.

Mass selected measurements of CO_2 emission were also carried out during abrasion. A polished calcite crystal was mounted about 3 cm from the ionizer of a quadrupole mass spectrometer and abraded with a diamond tip. The diamond was loaded with about 5 N and drawn back and forth across the crystal a distance of 1 cm in a linear motion. The abrasion during any given experimental run was confined to a narrow strip of calcite, resulting in a well developed "wear track."

To see if similar emission processes might accompany thermal stimulation of deformed material, time resolved measurements of CO_2 emission were made during the heating of a calcite powder. (The process of grinding produces extensively deformed particles.) A single crystal was ground in a glass beaker with a glass rod to create small crystallites less than 10 μm in diameter. This powder was promptly loaded into a vacuum system equipped with a Ta ribbon heater and pumped down. The heater was mounted about 1 cm from and in direct view of the quadrupole ionizer. A thermocouple attached to the heater provided a crude measure of the powder temperature. The temperature gradients in the powder imply that the measured temperature is a lower bound on the temperature of the powder as a whole.

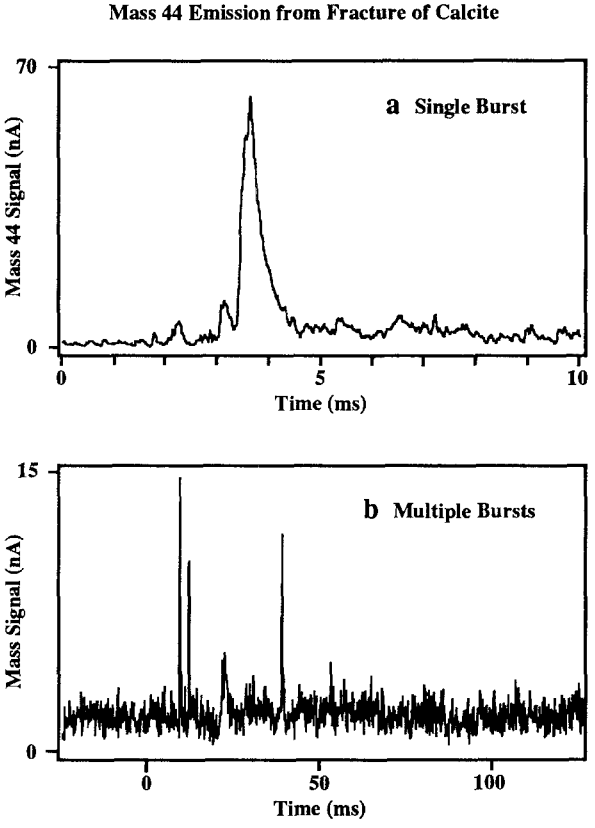

Fig. 1. Typical neutral emissions at 44 amu (CO_2^+) following fracture of calcite, **a** on a short time scale immediately after fracture, and **b** on a longer time scale to show subsequent bursts. Fracture occurred at time t=0

Results and Discussion

Fracture Experiments

Typical neutral emissions at 44 amu (CO_2^+) are shown in Fig. 1a. Most often a single burst was observed 2–4 ms after fracture. As shown in Fig. 1b, two or three bursts often follow. Occasionally, CO_2 bursts were observed as much as 100 ms after fracture. These bursts are quite narrow, typically 400 μs full width at half maximum. Measurements of gases occluded in polycrystalline materials indicate that the time between fracture and detection is typically about 60 μs (Dickinson et al. 1987). Therefore we attribute these emissions to CO_2 evolving from the sample after fracture. Similar but less intense emissions at 28 amu (CO^+) support the identification of the emitted product as CO_2. This signal is due to the dissociation of CO_2 by electron impact in the quadrupole ionizer. In the case of CO_2, the resulting signal at 28 amu is typically 10% of the signal at 44 amu. At the level of sensitivity employed, no emission was observed at 18 amu (H_2O^+), 32 amu (O_2^+) or 40 amu (Ca^+). The delayed mass 44 signals from fracture of $CaCO_3$ are therefore consistent with fracture-induced decomposition of $CaCO_3$ to CaO, yielding CO_2 as a volatile byproduct.

The delay of these emissions from fracture is of key importance with regard to the emission mechanism. The minimum observed delay, 2 ms, is far greater than any expected error in the measurement of the time of fracture (±10 μs). The delay is also far in excess of typical molecular flight times through the apparatus (100 μs, assuming a typical thermal velocity of 230 m/s). Thus the delay appears to be "real" in the sense that it is due to emission some milliseconds after the fracture event. The decay of the bursts are seen to be very rapid – on the same time scale as the pump-out time for CO_2 from the vacuum system.

The chief potential source of artifacts in this measurement is the ejection of particles from the fracture surface (ejecta) (Donaldson et al. 1988) which might subsequently strike the hot filament of the quadrupole ionizer (about 3000° C). This would yield CO_2 by rapid thermal decomposition. This source of CO_2 can be ruled out on two grounds. First, the velocity of such a particle would be too slow to reach the ionizer 2–4 ms after fracture. An upper limit on the velocity of ejected particles is given by the velocity of a calcite surface under the influence of a pressure pulse equal in magnitude to the stress at fracture. This velocity is given by $v_{max}=\sigma/\rho c$, where σ is the stress at the tensile face of the sample, ρ is the density of calcite (2.71 g/cm), and c is the longitudinal sound wave velocity (7200 m/s). The maximum tensile stress observed in this work is about 20 MPa, which corresponds to a maximum ejecta velocity of about 1 m/s. At this velocity, particles would require

at least 6 ms to reach the ionizer filament. Since the first emission bursts were consistently observed 2–4 ms following fracture, particle ejection cannot account for these bursts.

Further evidence against the thermal decomposition of ejected particles is the absence of emissions at 40 amu (Ca^+). The filament temperature is well above boiling point of CaO (2850° C), so that particles striking the ionizer filament would yield intense CaO signals. Although we did not monitor this signal directly due to the difficulty of tuning the quadrupole accurately to 56 amu, a strong signal at 40 amu (Ca^+) is also expected from CaO. For instance, emission at 40 amu was readily detected during high temperature *thermal* decomposition of calcite due to the sublimation of CaO. As no evidence of emission at 40 amu was observed to accompany fracture, we again rule out the thermal decomposition of ejected particles as a potential source of the observed CO_2.

The amount of CO_2 evolved in a single fracture is on the order of 5×10^9 molecules/cm^2 of fracture surface. Fox and Soria-Ruiz reported significantly greater amounts of CO_2 from the cleavage of calcite (2×10^{11} molecules/cm^2) (Fox and Soria-Ruiz 1970). This is probably due to the manner of fracture employed in their work, in which a cleavage blade was positioned on the sample and impacted to achieve a high crack velocity. This process is more violent than the three point bending employed in this work due to damage at the point of cleavage blade contact (Mathison et al. 1989). Fox and Soria-Ruiz attributed the observed CO_2 emission to fracture-induced heating of $CaCO_3$, resulting in thermal decomposition. However, any heating associated with crack growth would necessarily be a very prompt process, and would not account for the delay between fracture and the onset of CO_2 emission. The low time resolution of their measurements (on the order of 100 ms) was insufficient for the observation of the delay. We suggest that fracture-related decomposition is not directly a consequence of heating during crack growth, but results from the subsequent relaxation of deformation produced during crack growth.

Abrasion

CO_2 emission measurements were also made during the abrasion of a polished calcite crystal surface with a diamond tip. During abrasion, CO_2 bursts were observed, as well as a low intensity "continuum" component of emission. Figure 2a shows on a slow time scale the CO_2 signal accompanying several abrasion cycles. Note that after the last cycle, the small continuum component requires some seconds to decay. The total amount of emission is larger here compared with single fracture events due to the larger surface area of damage being produced in the abrasion process. A single burst of abrasion related emission is shown on a faster time scale in Fig. 2b. The individual bursts are again quite narrow, being comparable in shape to the fracture related bursts. Thus it is very likely that the processes involved in the production of CO_2 bursts during abrasion are similar to those accompanying fracture in three point bend.

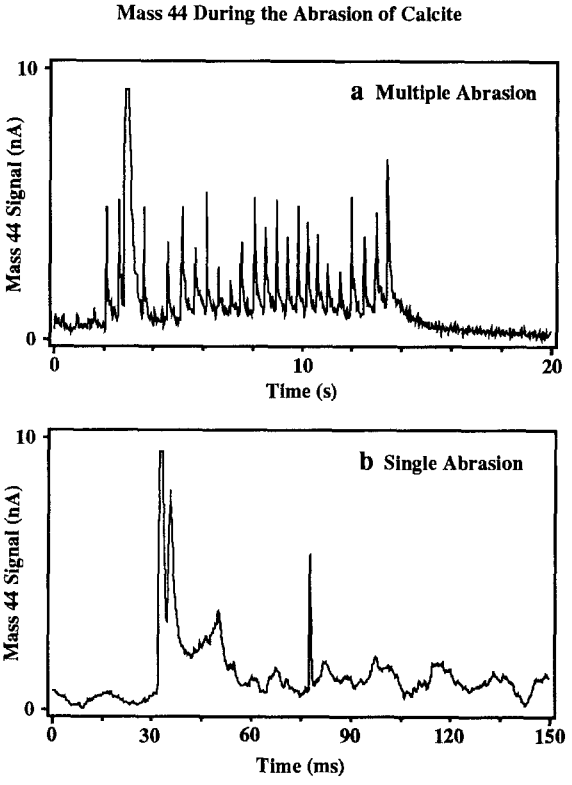

Fig. 2. CO_2 emission accompanying the abrasion of calcite with a diamond tip, **a** on a long time scale showing the bursts with repeated scratching, and **b** on a short time scale to show individual bursts

Heating Experiments

The process of grinding produces plastic deformation which would presumably remain to a great extent in the particles. Thus, heating powdered calcite created by grinding might induce CO_2 production at relatively low temperatures. Figure 3a shows the CO_2 evolution as a function of time; simultaneously recorded heater temperatures are indicated at various times. The heater current was raised in stages. The marked increase in CO_2 emission at temperatures on the order of 300–400° C is quite evident. CO_2 bursts are observed at temperatures above about 300° C. A few of these bursts are shown in Fig. 3b on a faster time scale, where the temperature was ~445° C. Most of these bursts were quite narrow, less than 1 ms FWHM. At these slow sampling rates (2 ms intervals) only the largest bursts were recorded on the digitizer. On even faster time scales, one typically observes 10^2–10^4 smaller, faster CO_2 bursts accompanying the steadily increasing, "continuum" component of CO_2 above 300° C. This is approximately the temperature at which dislocations become mobile in calcite (Anuradha and Bhagavan Raju 1986). Thus dislocations produced during grinding could begin to "pop out" at around 300° C, resulting in CO_2 bursts at this temperature, well below the nominal decomposition tempera-

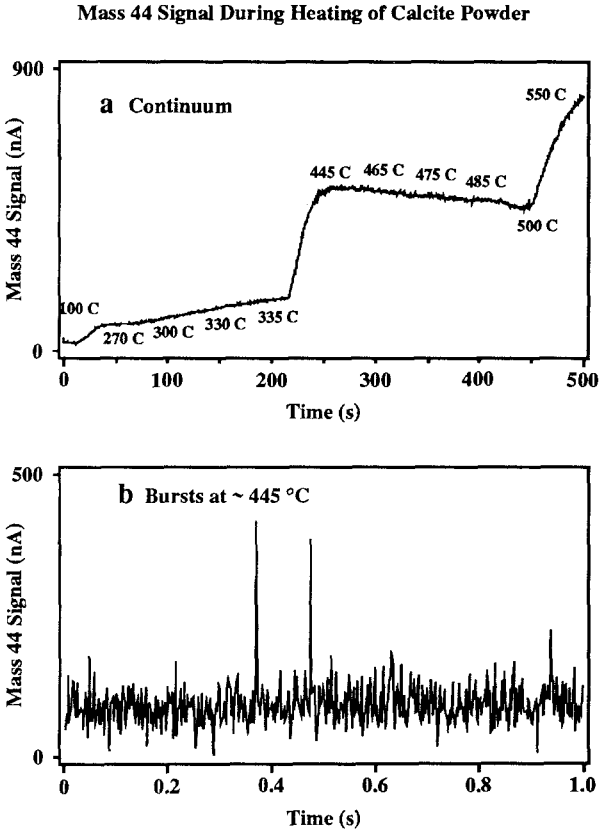

Fig. 3a, b. CO_2 emission during heating of pulverized calcite. **a** smoothed plot of emission during the temperature ramp. The temperature of the heater at successive stages of heating is indicated along the curve itself. The steep portions of the emission curve follow step increases in the heater current. **b** emissions on a faster time scale at a temperature ~445° C, showing frequent bursts

ture. We therefore propose that the dramatic response in overall CO_2 emission and the detection of numerous bursts with relatively mild thermal stimulation is due to the annealing of extensive plastic deformation in these particles.

Isothermal heating experiments at temperatures above 300° C showed an initial rise in emission, followed by a long slow decay. Although the data shown in Fig. 3a are not strictly isothermal, the tendency to saturate and decay is quite evident in the central portion of the diagram. If the temperature were subsequently lowered, emission would drop to low levels. Substantial emission would not be observed until the temperature was raised to levels comparable to the highest temperature previously experienced by that sample. This is consistent with the progressive annealing of damage with increasing sample temperature. Dislocations or twins which may be immobile at one temperature (due to defect pinning or other effects) may become mobile at higher temperatures.

Heating experiments were also attempted with macroscopic single crystals whose surfaces were abraded and indented in air. Similar low temperature CO_2 emissions were often observed (numerous bursts superimposed on a continuum); however some samples showed little emission until heated to about 800° C. We suspect that the crystals yielding little CO_2 at low temperatures lacked the required deformation structures. For instance, dislocations on some slip systems are known to have little effect on thermal decomposition, while dislocations on other slip systems greatly enhance decomposition (Thomas and Renshaw 1967).

Proposed CO_2 Emission Mechanism

In previous studies of the fracture of alkali halides, we observed delays between fracture and alkali emission similar to those observed in calcite. In alkali halides, the delay was attributed to the relaxation of fracture induced deformation. Fracture of alkali halides is known to involve the production of dislocations which are driven into the bulk material by the high stresses at the crack tip (Gilman et al. 1958; Burns and Webb 1966). Dislocation production is especially effective during slow crack growth, but dislocation-related deformation accompanies rapid crack growth as well (Swain et al. 1974; Forwood and Lawn 1966). After fracture, near-surface dislocations will be attracted back to the surface under the influence of an image force. Simple models of dislocation motion indicate that the process of attraction to the free surface can result in the emergence of dislocations hundreds of ms after the completion of fracture (Dickinson et al. 1991a). Furthermore, dislocation "popout" can release several keV energy, sufficient for the emission of thousands of alkali-containing molecules. The emission of greater quantities (we observed typically 10^7–10^8 alkali-containing atoms and molecules per burst) probably involves the breakdown of more complex dislocation structures such as pileups.

The deformation of calcite at room temperature generally precedes by a different mechanism that that of the alkali halides undergoing twin formation rather than dislocation motion (Kaga and Gilman 1969). The application of an appropriately oriented shear stress at room temperature produces a narrow region of twinned material. This material can be "detwinned" by the application of an oppositely directed shear stress of sufficient magnitude. Detwinning of macroscopic twins can also occur spontaneously over periods of hours or days if the twinning stress is removed. Although we are unaware of experimental observations of twinning on calcite fracture surfaces, imperfect twins have been observed on germanium fracture surfaces (Suzuki and Kamada 1966). Thus it is reasonable to assume that small regions of twinned material are formed during fracture, and that they could detwin afterwards over time periods of milliseconds. This detwinning process, if sufficiently concerted, could result in localized deposition of energy at the surface and produce CO_2 emission. Alternatively, near-surface dislocations produced in the twinning/detwinning process could emerge after fracture, yielding emissions by a process similar to that described above for the alkali halides. Although dislocations are typically less mobile in calcite than in the alkali halides, they are produced in copious quantities during twinning (Kaga and Gilman 1969; Barber and Wenk 1979). If such dislo-

cations are sufficiently near the fracture surface, they may still be able to participate in popout processes. Thus, we attribute the observed emissions to the relaxation of fracture-related deformation involving either small regions of twinned material or their associated dislocations. Although rapid, highly localized heating during these relaxation processes may be responsible for the CO_2 bursts, measurements of the translational energy of the fracture induced bursts from single crystal Ge (Dickinson et al. 1991 b) and from alkali halides (Dickinson et al. 1991 c) indicate temperatures far below sublimation temperatures. Thus, we suspect that non-thermal processes dominate these relaxation driven emission processes.

Deformation may promote decomposition by providing the required energy (kinetic and potential) and by providing a favorable molecular arrangement for coupling this energy into carbonate ions. Simulations of dislocation popout in the alkali halides suggests that a significant amount of kinetic energy can be deposited in the surface region as rapidly moving dislocation approaches from below. Symmetry suggests that analogous decomposition-like reactions occur during dislocation/twin formation as well as relaxation, due to the necessary molecular rearrangements in the shearing processes. However, decomposition is reversible unless the product CO_2 is allowed to escape, and escape is hindered until the fracture surface is formed. Thus we expect significant releases of CO_2 only upon relaxation of the deformation (detwinning or dislocation popout). High densities of appropriately oriented dislocations accelerate calcite decomposition, as noted above. Dislocations can reduce the apparent activation energy for thermal decomposition from about 2.2 eV per $CaCO_3$ molecule to about 1.2 eV per molecule (Thomas and Renshaw 1967; Darroudi and Searcy 1981). Decomposition stimulated by the relaxation of plastic deformation would be greatly facilitated by similar geometric effects. Even more favorable geometries probably occur during dislocation motion or (de)twinning, which require more energetic but transient states. Thermal decomposition presumably involves similar transient states, which would be produced by thermal vibrations alone.

Similar processes are probably responsible for the CO_2 bursts observed during abrasion. The continuum component of emission requires further explanation. Much of the continuum emission can be attributed to the slow escape of CO_2 from the network of narrow cracks produced during abrasion. However, we expect that delayed crack growth may contribute significantly. The residual stresses in the wake of the diamond tip can be quite high, and it is not uncommon for some of these stresses to relax by crack growth. In indentation experiments on glass, radical cracks are commonly observed to grow during the *removal* of the indenter (Lawn et al. 1983). Crack growth after the passage of the indenter would extend into the deformed material below, providing a free surface and thereby promoting further relaxation by dislocation motion to the free surface or detwinning in the adjacent material. In MgO, substantial evidence suggests that crack growth through deformed material can lead to significant relaxation of the deformation by dislocation popout at the newly created fracture surface (Yoo et al. 1984). The corresponding process in calcite would very likely result in local decomposition and CO_2 emission into growing microcracks.

Lange and Ahrens (1986) found that calcite decomposition accompanying high velocity impact is often largely concentrated within shear bands. Under these conditions, localized heating at shear bands may be significant, so that both thermal and mechanical effects may play important roles in high impact induced decomposition of calcite.

Any decomposition accompanying cleavage would naturally result in a less than perfect fracture surface. Such defects can be chemically active, with important implications for chemisorption and catalytic reactions. The low volatility of the CaO associated with these defects suggests that it would remain on the surface. Given the relatively small amount of CO_2 emission observed, the density of such defects appears to be low. This is consistent with *X-Ray Photoelectron Spectroscopy* (XPS) measurements of the oxygen 1 s level on calcite cleavage surfaces, which showed no evidence of Ca-O bonding (Baer et al. 1991). In this experiment, the calcite was cleaved by pressing a blade against the crystal until cleavage occurred. Since this is most similar to Fox and Soria-Ruiz' method of fracture, we use their results to estimate 1 decomposition event per 2500 surface carbonate ions. The correspondingly small amount of CaO formed would be below the sensitivity of XPS measurements. Nevertheless, recent XPS measurements show evidence of line broadening on fresh cleavage surfaces. The broadening is not observed after dipping the sample in water, which is expected to dissolve CaO (Baer et al. 1991). Thus, line broadening may be indicative of surface disorder, to which decomposition during cleavage undoubtedly contributes significantly. Other workers (Stipp and Hochella 1991) have recently reported evidence for carbide and CO_3H groups on calcite surfaces created by cleavage in ultra high vacuum.

Conclusion

The observation of delayed CO_2 emission following the fracture of calcite and the CO_2 emission accompanying low temperature annealing of highly damaged calcite crystallites suggest that the decomposition process is largely mechanical in origin, and not due to heat generated during crack growth. The mechanical processes of twinning and/or dislocation motion apparently involve molecular motions which promote the decomposition of the carbonate anion. During the relatively "gentle" fracture process described here, significant release of CO_2 occurs only during the relaxation of this deformation. A detailed understanding of the atomic and molecular processes involved in decomposition will probably require molecular dynamics simulations of the calcite structure. The coupling of mechanical energy into electronic or chemical processes can have important implications, for instance, in the ignition of shock-sensitive exo-

thermic chemicals. The role of dislocations and twinning also suggest several lines of investigation of factors controlling the decomposition process. For instance, impurities which impede the formation of twins or dislocation motion may inhibit decomposition, whereas specific kinds of deformation may promote it.

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