

Volcanic edifice weakening via decarbonation: A self-limiting process?

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[1] The inherent instability of volcanic edifices, and their resultant propensity for catastrophic collapse, is a constant source of volcanic risk. Structural instability of volcanic edifices may be amplified by the presence of carbonate rocks in the sub-volcanic strata, due to the debilitating response of carbonates to thermally-induced alteration. Nonetheless, decarbonation reactions (the primary weakening mechanism), may stall when the system becomes buffered by rising levels of a reaction product, carbon dioxide. Such thermodynamic stalling might be inferred to serve to circumvent the weakness of volcanic structures. However, the present study shows that, even when decarbonation is halted, rock physical properties continue to degrade due to thermal microcracking. Furthermore, as a result, the pathways for the escape of carbon dioxide are numerous within a volcanic edifice. Therefore, in the case of an edifice with a sub-volcanic sedimentary basement, the generation of carbon dioxide via decarbonation is unlikely to hinder its impact on instability, and thus potentially devastating flank collapse. **Citation:** Mollo, S., M. J. Heap, G. Iezzi, K.-U. Hess, P. Scarlato, and D. B. Dingwell (2012), Volcanic edifice weakening via decarbonation: A self-limiting process?, *Geophys. Res. Lett.*, 39, L15307, doi:10.1029/2012GL052613.

1. Introduction

[2] Sub-volcanic carbonate basements are common (e.g., Mt. Etna, Mt. Vesuvius, the Colli Albani volcanic district, the Campi Flegrei volcanic district (all Italy), Popocatepetl volcano (Mexico), Yellowstone volcanic system (USA), and Merapi (Indonesia)). Volcanic edifices are inherently unstable [Acocella and Puglisi, 2010]. Their propensity for failure and collapse provides a constant threat to those who live within the shadow of an active volcano. The integrity of the sub-volcanic foundation is likely to play a key role in edifice instability [Van Wyk de Vries and Borgia, 1996]. Recent studies have highlighted that volcanoes with a carbonate sub-volcanic basement may be especially prone to instability, due to their susceptibility to debilitating thermally-induced alteration [Mollo et al., 2011a; M. J. Heap et al.,

Calcination-driven weakening of the carbonate basement under Mt. Etna volcano (Italy): Implications for volcano instability, submitted to *Journal of Volcanology and Geothermal Research*, 2012]. The experiments of Mollo et al. [2011a] and Heap et al. (submitted manuscript, 2012) were however performed in an “open” system where the gaseous products generated by thermal decomposition could readily escape. While this provides useful primary insight, the most debilitating chemical reaction – the decarbonation of calcium carbonate ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) – might be arrested when the CO_2 concentration in the system is high [Khinast et al., 1996; Wang and Thomson, 1995; Samtani et al., 2002]. In such a “closed” system, where decarbonation is hindered, rock physical properties might be expected to suffer less and edifice stability could therefore be less compromised than previously anticipated. To this end, and to compliment the data of Mollo et al. [2011a] and Heap et al. (submitted manuscript, 2012), we have performed a suite of high-temperature decarbonation experiments on carbonate rock under controlled CO_2 conditions (i.e., to reproduce the conditions of an “open” and a “closed” system). The resultant samples were then assessed in terms of their chemical and physical properties. We discuss these data in terms of volcano stability.

2. Materials and Methods

[3] For the purpose of this investigation, we use Mt. Etna volcano (Southeast Sicily, Italy) as a case study. Mt. Etna represents an ideal candidate for our study. (1) It is the largest (45 km wide stratovolcano standing 3.3 km above sea level), most active, and best-monitored volcano in Europe. (2) The thin basaltic cover rests on a vast (10 km thick) sub-volcanic carbonate basement, i.e., the Hyblean Plateau [Lentini, 1982]. (3) The Hyblean Plateau is exposed to high temperatures as a result of proximal magma storage volumes [e.g., Tibaldi and Groppelli, 2002; Bonforte et al., 2009; Bonaccorso et al., 2010]. Additionally, Etnean magmas are considered to be stored at extremely high temperatures, ranging from 1200 to 1150°C [Del Gaudio et al., 2010; Mollo et al., 2010a, 2011b]. The material used in this study was Mt. Climiti limestone (MCL), from the thick-bedded bio-calcarene units in the Monti Climiti Formation of the Sortino Group, i.e., within the carbonates of the Hyblean Plateau [Grasso and Lentini, 1982]. Cylindrical core samples (25 mm in diameter and 50–60 mm in length) were prepared from the same set of blocks as in Heap et al. (submitted manuscript, 2012). The MCL of this study had an initial connected porosity of 0.32 and was essentially 100 wt.% calcite.

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[4] Decarbonation experiments were conducted in a vertical tube gas-mixing furnace at the HP-HT Laboratory of Experimental Volcanology and Geophysics at the Istituto Nazionale di Geofisica e Vulcanologia (INGV, Rome). According to Le Chatelier's principle, the presence of CO_2 should be the main rate-limiting factor of the decarbonation of calcite, irrespective of the amount of carbonate material and the grain particle size [Khinast *et al.*, 1996; Wang and Thomson, 1995; Samtani *et al.*, 2002]. From a thermodynamic point of view, it is the carbon dioxide fugacity ($f\text{CO}_2$) rather than the CO_2 partial pressure that governs the chemical equilibrium of decarbonation [Wenzel *et al.*, 2002; Barnes *et al.*, 2005; Mollo *et al.*, 2010b; Di Rocco *et al.*, 2012]. Magma chambers emplaced in carbonate substrate: Petrogenesis of skarn and cumulate rocks and implication on CO_2 -degassing in volcanic areas, submitted to *Journal of Petrology*, 2012]. In our decarbonation experiments we therefore chose to vary the $f\text{CO}_2$ of the system. This means that the progression of the decomposition of a carbonate rock (η_{dec}) should be inversely proportional to the $f\text{CO}_2$ of the system. The η_{dec} value represents the ratio of the CO_2 released during CaCO_3 partial decomposition to the total CO_2 content at the end of the reaction, and will range from 0 to 1 (i.e., $\eta_{\text{dec}} = 1$ means that all the CaCO_3 has fully decomposed). Our experimental samples were first inserted into a Pt-coil and then suspended within the hot zone of the furnace. The $f\text{CO}_2$ was imposed using a gas mixture of $\text{CO}_2 + \text{CO} + \text{air}$. In this study we reproduced the conditions expected for (1) an "open" system where the CO_2 can be rapidly and efficiently removed ($\log f\text{CO}_2 = -4.41$) and, (2) a "closed" system where the CO_2 cannot escape ($\log f\text{CO}_2 = -3$ to -1.01). Although the system can be considered "closed", we ran experiments at $\log f\text{CO}_2 = -1.01$, -2.00 , and -3.00 in order to assess any potential impact on rock physical and chemical properties. A target temperature of 750°C was reached using a constant heating rate of $10^\circ\text{C}/\text{min}$, to minimise thermal shock in the samples [Mollo *et al.*, 2011a]. For each $f\text{CO}_2$ we ran two experiments, one where the sample was kept at the target temperature for 2 hours, and another for 12 hours. The samples were then cooled at the same rate ($10^\circ\text{C}/\text{min}$). This target temperature was guided by the thermogravimetric (TG) analyses of Heap *et al.* (submitted manuscript, 2012) who showed that, for MCL, CaCO_3 starts to decompose at temperatures above 680°C , and has a strong endothermic peak at 860°C . The wt.% of CO_2 released from the rock during the decarbonation process was calculated at the end of each experiment.

[5] In order to understand the impact of the temperature at which decarbonation has been observed to ensue under variable $f\text{CO}_2$ (i.e., "open" and "closed") conditions on rock physical properties, we determined the porosity, ultrasonic velocities, V_p/V_s ratio, dynamic elastic moduli, and the uniaxial compressive strength (UCS) of our test samples. Porosity measurements were performed using the triple-weight water saturation method. Ultrasonic velocities were measured using an Agilent Technologies DSO5012A digital storage oscilloscope, an Agilent Technologies 33210A, 10 MHz function/waveform generator and two broadband PZT piezoelectric transducer crystals (100 kHz to 1 MHz frequency) located at the top and bottom of the sample. All measurements were collected under a force of 600 N to ensure a good contact between the endcaps and the sample.

Ultrasonic velocities were subsequently used to calculate the dynamic Young's modulus (E_d) and the dynamic Poisson's ratio (ν_d) [Guéguen and Palciauskas, 1994]. Finally, UCS experiments were performed on the samples using the uniaxial press at the Laboratoire de Déformation des Roches (LDR, Université de Strasbourg). Samples were loaded at a constant strain rate of $1.0 \times 10^{-5} \text{ s}^{-1}$ until failure. Axial strain and force were continuously monitored during experimentation by means of an LVDT transducer and a load cell, respectively.

[6] The impact of decarbonation under different $f\text{CO}_2$ conditions (i.e., "open" and "closed") conditions on the chemical properties of our test samples was achieved by thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses [carried out at the Sektion Mineralogie, Petrologie und Geochemie (SMPG) of Ludwig Maximilians Universität (LMU) in Munich (Germany) using a Netzsch STA 449 C thermobalance apparatus] and X-ray powder diffraction pattern (XRPD) analyses [performed at the DIGAT department of Università G. d'Annunzio in Chieti (Italy) by means of a Siemens D-5005 diffractometer; the collected data were then used for determining the quantitative mineral phase amounts by the Rietveld method.]. Finally, microstructural analyses were carried out using the JEOL-JSM6500F Field Emission Gun - Scanning Electron Microscope (FE-SEM) located at the HP-HT Laboratory in Rome (INGV).

3. Results and Discussion

[7] MCL rock physical properties (porosity, ultrasonic wave velocities, V_p/V_s , UCS, and dynamic elastic moduli) are plotted as a function of η_{dec} (carbonate decomposition progression, see above) in Figure 1 for the experiments held at 2 hours (grey circles), those held at 12 hours (white circles), and for the "as-collected" material (black squares). The CO_2 emission calculated for each sample is also presented in Figure 1a. Our data illustrates that rock physical properties showed a progressive deterioration, and that the wt.% of CO_2 emission increased, as η_{dec} increased.

[8] In the "open" system, the thermal dissociation of CaCO_3 progressed and the value of η_{dec} reached 0.38 after 2 hours (releasing 9.85 wt.% of CO_2) and 1.0 after 12 hours (releasing 42.48 wt.% of CO_2). After 2 hours ($\eta_{\text{dec}} = 0.38$), MCL rock physical properties had deteriorated and, after 12 hours ($\eta_{\text{dec}} = 1$), they were drastically altered from the "as-collected" material ($\eta_{\text{dec}} = 0$) (Figure 1). After 12 hours, the V_p , V_s , UCS, and dynamic Young's modulus decreased by 61, 66, 64, and 89%, respectively; whereas the porosity, V_p/V_s ratio, and Poisson's ratio increased by 28, 13, and 24%, respectively. The axial stress-strain curve for the experiment held for 12 hours is shown in Figure 2. The curve shows that, although there was substantial post-peak strain-softening, the deformation behaviour was still brittle. Sample failure was sluggish and there was no clear stress drop, although the mode of failure was axial splitting (see inset on Figure 2). Our chemical and mineralogical analyses (a combination of TG, DSC, and XRPD analyses) indicated that, under "open" conditions, a new hydrous phase (i.e., portlandite) and CaO (i.e., lime) formed at the expense of calcite (Figure 3). The amount of calcite progressively decreased, and hence the amount of portlandite and lime increased, as η_{dec} increased (Figure 3), reflecting the progress

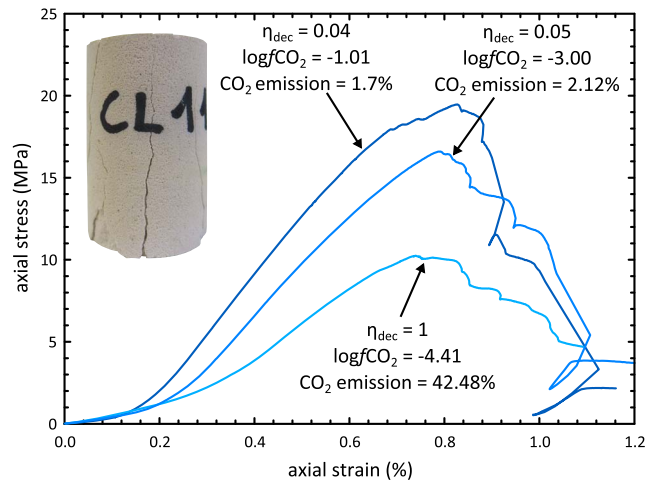
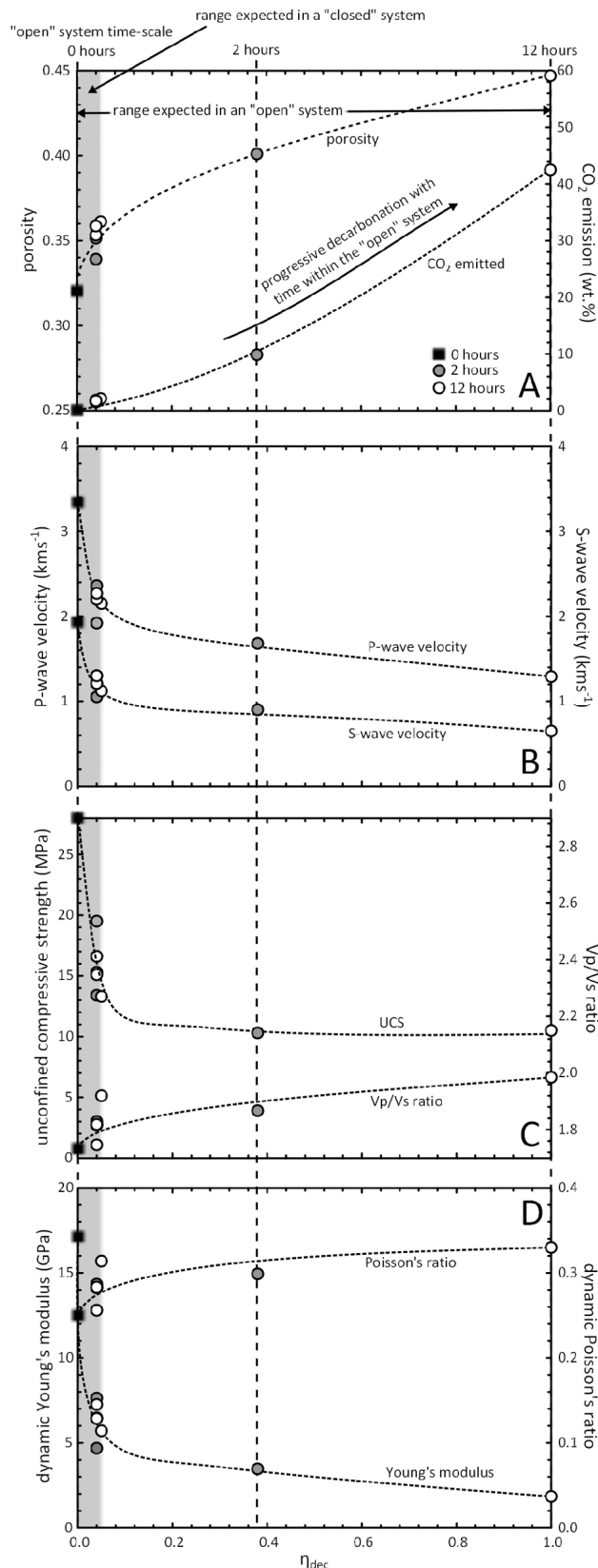


Figure 2. Constant strain rate, uniaxial stress-strain curves for Mt. Climiti limestone. Two curves are for samples decarbonated under a “closed” system ($\eta_{\text{dec}} = 0.04$ and 0.05), and one curve is for a sample fully thermally-decomposed under an “open” system ($\eta_{\text{dec}} = 1$).

of the decarbonation reaction. Portlandite was the most abundant mineral phase at $\eta_{\text{dec}} = 1$. Portlandite (a calcium hydroxide) forms by the recombination of CaO (from the decomposition of CaCO_3) with water vapour in air according to the reaction: $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$. The formation of portlandite in decarbonated limestones was previously observed by Mollo *et al.* [2011a] and Heap *et al.* (submitted manuscript, 2012). In contrast to the close-packing of carbonate groups, with calcium present in rhombohedral calcite grains, portlandite has a hexagonal layered crystal structure of calcium oxide layers separated by hydrogen, resulting in a weak interlayer attraction. Therefore, the formation of portlandite drastically influences both microstructure and strength [Nourredine, 2011; Mollo *et al.*, 2011a]. The textural changes caused by such thermal decomposition were imaged using a backscattered SEM. After 12 hours in the “open” system (i.e., $\eta_{\text{dec}} = 1$), the microstructure had been greatly altered (Figure 4a). The grains (a mixture of portlandite and lime) appear to have been partly dissolved, giving the rock a “sponge-like” texture. The number and dimension of the cavities drastically increased, explaining the large increase in porosity (from 0.32 to 0.45). Our approach has shown that, in an “open” system, decarbonation (and the subsequent formation of portlandite) can take place and leads to severe chemical, mineralogical, and textural changes that greatly impact rock physical properties.

Figure 1. The influence of the progression of decarbonation (η_{dec}) on the physical properties of Mt. Climiti limestone. (a) Porosity. (b) P- and S-wave velocities. (c) Unconfined compressive strength and Vp/Vs ratio. (d) Dynamic Young’s modulus and Poisson ratio. The CO_2 emission is also shown in A. The physical properties achievable within a “closed” system are confined to the grey region, while the entire plot represents those achievable within an “open” system. The black squares represent the “as-collected” material, and the grey and white circles represent an experiment with a 2 and 12 hour duration, respectively.

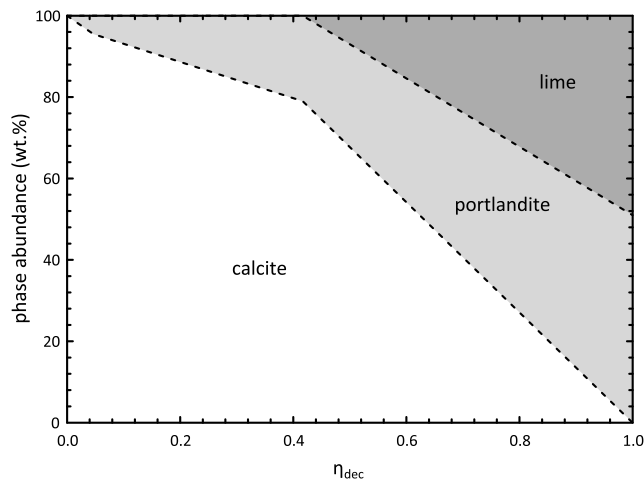


Figure 3. The influence of the progression of decarbonation (η_{dec}) on the modal composition of Mt. Climiti limestone, as mapped out using a combination of TG, DSC, and XRPD analyses.

[9] However, our experiments reproducing “closed” system conditions all resulted in very low values of η_{dec} (0.04–0.05), even after 12 hours (Figure 1; “closed” system experiments are limited to the grey region). During this time the CO_2 emitted from the samples was only ≤ 2.12 wt.%, attesting to the fact that the decarbonation process was essentially stifled by the high f_{CO_2} conditions. Chemical and mineralogical analyses all indicated that, between $\eta_{\text{dec}} = 0.04$ –0.05, there was mainly calcite present in the sample (Figure 3), and backscattered SEM images (for $\eta_{\text{dec}} = 0.04$) showed that there was little change to the rock microstructure, although some microcracks were present (Figure 4b). At $\eta_{\text{dec}} = 0.04$, the rock texture was characterized by a network of calcite grains with sparse inter- and intra-crystal sub-round cavities. However, MCL rock physical properties were still affected under such “closed” conditions (Figure 1). The V_p , UCS, and dynamic Young’s modulus decreased by 34, 43, and 62%, respectively; whereas, relative to the initial properties of the “as-collected” material, porosity and Poisson’s ratio increased by 9 and 10%, respectively. The axial stress-strain curves for two samples (with η_{dec} values of 0.04 and 0.05) showed qualitatively similar behaviour as for the fully-decomposed sample (Figure 2). The samples still showed a large degree of post-peak strain-softening, but were ultimately brittle and failed by axial splitting (see inset on Figure 2). However, sample failure was marked by a more obvious stress drop. Since we can rule out severe chemical changes through decarbonation (η_{dec} values between 0.04 and 0.05 still indicate that some decarbonation took place), the source of these changes must be explained by another mechanism. The most likely mechanism responsible is thermal microcracking, perhaps prompted by the mild decarbonation. Thermal microcracks will have formed as a result of the build-up of internal stresses due to the thermal expansion anisotropy of calcite; indeed, at 750°C , the calcite cell-unit volume expands by more than 2% [Chang *et al.*, 1996]. Thermal microcracks have been previously observed to develop in carbonate rocks above temperatures of 200°C [Homand-Etienne and Troalen, 1984]. This hypothesis is supported by the observation of microcracks in the

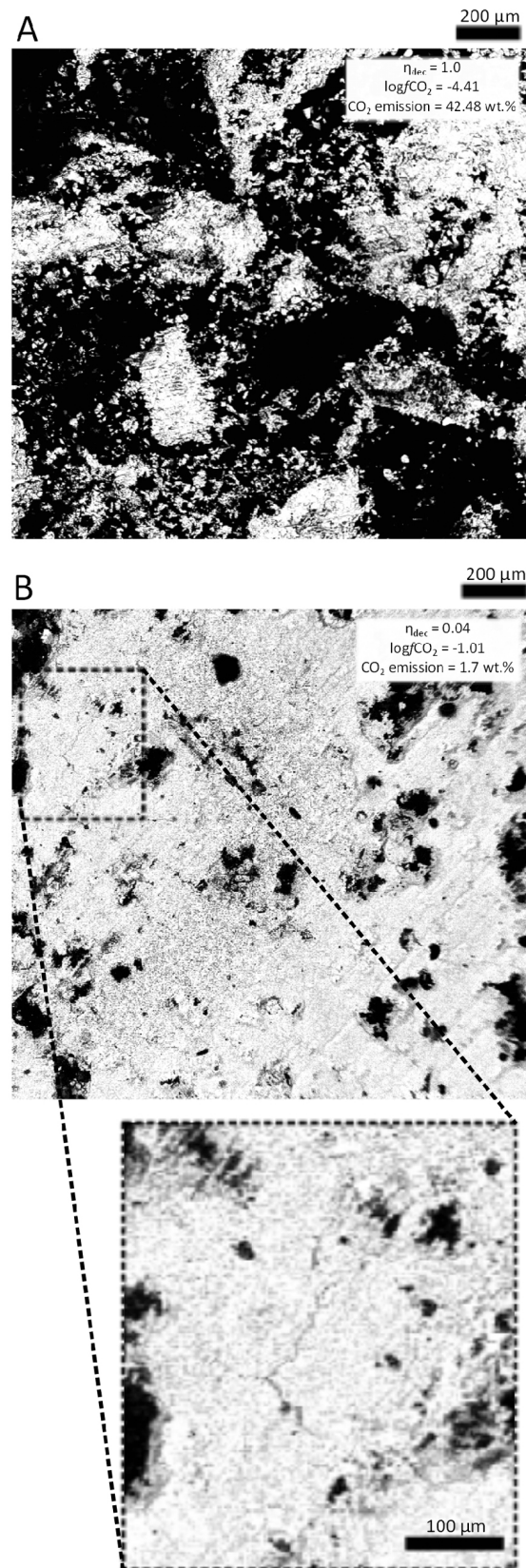


Figure 4. Backscattered SEM images of Mt. Climiti limestone test samples. (a) A fully thermally-decomposed sample ($\eta_{\text{dec}} = 1$; i.e., an “open” system). (b) A partially-decomposed sample ($\eta_{\text{dec}} = 0.04$; i.e., a “closed” system). The inset shows a zoomed-in image of a thermal microcrack.

backscattered SEM image of Figure 4b. These analyses show that, although the decarbonation was halted under such “closed” conditions, and therefore the chemical and mineralogical properties of the rock were largely unaffected, the rock physical properties still suffered as a result of thermal microcracking.

[10] Our results show that decarbonation within an “open” system permits the greatest changes in rock physical properties. However, rock physical properties also deteriorate in a “closed” system, due to thermal microcracking [see also Yavuz *et al.*, 2010, and references therein]. The thermal microcracking within a “closed” system would quickly convert it to an “open” system (since thermal microcracking has been previously shown to dramatically increase permeability, see Jones *et al.* [1997]). Therefore, given time, CO₂ will be quickly and efficiently removed in both scenarios, fuelling decarbonation, and resulting in detrimental changes to rock physical properties.

[11] We propose the following implications of these data for a volcanic edifice with a sub-volcanic sedimentary basement. As explained above, even if the decarbonation process is arrested in a “closed” system, rock physical properties, and therefore edifice stability, will still suffer due to thermal microcracking and the subsequent “opening” of the system. However, perhaps the existence of a “closed” system in a volcanic edifice is a somewhat unrealistic scenario. Volcanic rocks are often porous, permeable [Mueller *et al.*, 2005], and contain a high degree of microcracking [Vinciguerra *et al.*, 2005; Heap *et al.*, 2011]. Further, volcanoes are often home to large-scale fault systems that can act as effective pathways for degassing (e.g., the Pernicana fault at Mt. Etna [Giammanco *et al.*, 1998]). To return to our case study, the amount of CO₂ outgassed from Mt. Etna volcano makes it one of the largest CO₂-producing volcanoes in the world. However, only 13 Mt of the total yearly output (25 Mt) comes from the summit craters, the rest degasses from its flanks through active faults [Bruno *et al.*, 2001, and references therein]. Further, the large amounts of CO₂ that are emitted diffusely from the soil, or dissolved into Etnean aquifers, suggests that pure CO₂ and CO₂-saturated brines can move up along deep fractured zones [Giammanco *et al.*, 1998; Federico *et al.*, 2011]. It is well known that CO₂ is exsolved and released by ascending magma, due to its abundance and low solubility in silicate melts [Freda *et al.*, 2008, and references therein]. However, the assumption that CO₂ degassing at Mt. Etna is entirely magmatic in origin leads to a gross overestimate of the volume of magma during pre-eruptive ascent [D'Alessandro *et al.*, 1997]. This implies that a significant fraction of the volume of CO₂ outgassed from Mt. Etna must come from a “non-magmatic source”. Indeed, it has been recently suggested that the carbon isotopic signature of volcanic CO₂ from Mt. Etna could have a crustal origin related to the interaction of carbonates with hot mantle-derived magmas [Chiodini *et al.*, 2011]. For example, a rise in $\delta^{13}\text{C}$ has been recently measured at Merapi volcano (Central Java) and was attributed to a considerable addition of crustal CO₂ that supplemented the mantle-derived volatile flux, intensifying and sustaining the 2006 eruption [Troll *et al.*, 2012]. It therefore seems likely that the permeable nature of a volcanic edifice at Mt. Etna provides ample pathways for the CO₂ produced during decarbonation to escape (i.e., an “open” system), which will facilitate further decarbonation.

Therefore, we propose that Mt. Etna volcano is at significant risk for decarbonation-driven instability.

[12] Since the physical and mechanical properties of basaltic rocks from Mt. Etna volcano do not significantly change at relatively high (up to 800°C) temperatures [Mollo *et al.*, 2011a], the thermal-weakening of the carbonate basement rocks may be interpreted as one of the main processes altering the structural integrity of the volcano. Indeed, accelerated flank movements are commonly observed to follow magmatic events within the sub-volcanic basement at Mt. Etna [Walter *et al.*, 2005], highlighting the intimate relationship between the heating of the carbonate basement and the instability of the volcanic edifice. Further, long-term records of CO₂ degassing at Mt. Etna has also shown that high soil CO₂ fluxes are strictly related to the dynamics of magma ascent, a marked sliding of the eastern flank, and increased seismicity [Federico *et al.*, 2011]. It emerges therefore that carbonate basement decomposition at Mt. Etna may be the origin of low ultrasonic wave velocity zones [cf., Patanè *et al.*, 2006], preferential sliding surfaces [Froger *et al.*, 2001; Neri *et al.*, 2004; Lundgren *et al.*, 2004], the large-scale ESE seaward sliding of the eastern flank [e.g., Palano *et al.*, 2009; Heap *et al.*, submitted manuscript, 2012], and crustal-derived CO₂ emissions [Chiodini *et al.*, 2011; Heap *et al.*, submitted manuscript, 2012]. We deduce that similar processes could be operative at high-risk volcanoes with sub-volcanic carbonate basements worldwide.

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