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Direct quartz-coesite transformation in shocked porous sandstone from Kamil Crater (Egypt)

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ABSTRACT

Coesite, a high-pressure silica polymorph (pressure 3–10 GPa, temperature <3000 K), is a diagnostic feature of shock metamorphism associated with impact cratering on quartz-bearing target rocks. It is preserved as a metastable phase in sedimentary target rocks that experienced peak pressures in excess of ~10 GPa, where it typically occurs as intergranular polycrystalline aggregates of microcrystals embedded in silica glass known as "symplectic regions." The presence of coesite in the symplectic regions of rocks experiencing shock conditions beyond the limits of the coesite stability field is a controversial issue. Through a combined scanning and transmission electron microscopy and Raman spectroscopy study of shocked quartzarenites from the 45-m-diameter Kamil Crater (southwest Egypt), we show that coesite in symplectic regions forms through direct subsolidus transformation from quartz, in contrast with the prevailing hypothesis for crystalline targets. The quartz-to-coesite transformation takes place during localized shock-wave reverberation at the beginning of the pore collapse process. Complete pore collapse generates the high temperature regimes responsible for the subsequent production of the embedding silica melts, in part at the expense of the previously formed coesite. This work documents the role of pore collapse in producing localized pressure-temperature-time gradients in shocked porous targets, as predicted by numerical models in the literature.

INTRODUCTION

Our understanding of the nature and mechanism of high-pressure phase transformations by shock waves generated by meteorite impacts stems from the effective synergy among the experimentally determined Hugonoit equations of state, direct observation of materials recovered from shock experiments, and the study of natural impactites. The difference in time scale (several orders of magnitude) between shock experiments (<1 µs) and natural impacts (from milliseconds to seconds) can lead to major differences between experimentally induced mineral transformations and those observed in natural shocked rocks. Pristine natural impactites, providing ground truth, are of crucial importance in addressing these debated differences.

Coesite is a high-pressure silica polymorph that is thermodynamically stable at pressures of 3–10 GPa and temperatures less than ~3000 K. In terrains where an endogenic origin can be ruled out, it is one of the diagnostic indicators of shock metamorphism in quartz-bearing target rocks (French and Koeberl, 2010).

Coesite has been described in a dozen of the ~190 impact sites known on Earth, regardless of the scale of the impact structure, from Vredefort (South Africa; Martini, 1991) to Kamil (southwest Egypt; Fazio et al., 2014). At these sites, it is preserved as a metastable phase in non-porous crystalline rocks that experienced peak shock pressures above ~30–40 GPa, and in porous sedimentary rocks shocked at pressures as low as ~10 GPa (e.g., Stöffler and Langenhorst, 1994; Kowitz et al., 2016). In the latter rocks, it typically occurs in trace amounts as microcrystalline aggregates in silica glass (diaplectic or impact melt glass) located in intergranular pockets and veins. These domains, known in the literature as "symplectic regions" (Kieffer et al., 1976), are interpreted as collapsed pores where spikes in pressure and temperature associated with closure of the pores created the conditions for the formation of high-pressure silica phases. This explains the localized formation of coesite in porous sedimentary rocks at shock pressures significantly lower than in crystalline rocks (e.g., Kieffer et al., 1976) and different from that of equilibrium stability. The actual mechanism whereby coesite forms in these symplectic regions, i.e., direct transformation from quartz or crystallization from hot silica melts jetted into the collapsing pore (Kieffer et al., 1976), is still unclear.

Symplectic regions were identified in shocked sandstone ejecta samples from the 45-m-diameter, younger-than 5 ka Kamil Crater (Fig. 1; Folco et al., 2010) and preliminarily characterized in a previous work (Fazio et al., 2014). The exceptional state of preservation of Kamil Crater and, in particular, the lack of evidence for post-shock thermal overprint and alteration due to hydrothermal activity typically observed in shock metamorphic rocks from larger impact structures (e.g., Martini, 1991; Fazio et al. 2017), prompted us to test current models for formation of coesite in symplectic regions through combined scanning electron microscopy, Raman spectroscopy, and electron diffraction microstructure analysis.

SAMPLES AND METHODS

The coesite-bearing symplectic regions studied in this work are from a fist-sized shocked sandstone ejecta sample (L23) from Kamil Crater. The sample was collected ~350 m from the crater rim in the main downrange ejecta ray (Fig. 1) during the 2010 Italian/Egyptian geophysical expedition (Fazio et al., 2014). Two polished thin sections were prepared for mineralogical and petrographic investigation by optical microscopy, Raman spectroscopy, and field emission gun–scanning electron microscopy (FEG-SEM). One section was used to extract portions of the sample for nanopetrographic and crystallographic analyses of silica phases by

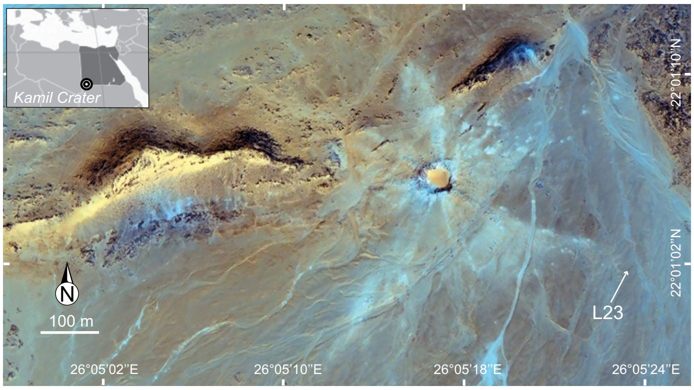

Figure 1. The 45-m-diameter Kamil Crater, Egypt (22°01′06″N, 26°05′15″E; QuickBird satellite image), showing collection site of the sandstone ejecta sample (L23) studied in this work.

GSA Data Repository item 2018269 | https://doi.org/10.1130/G45116.1

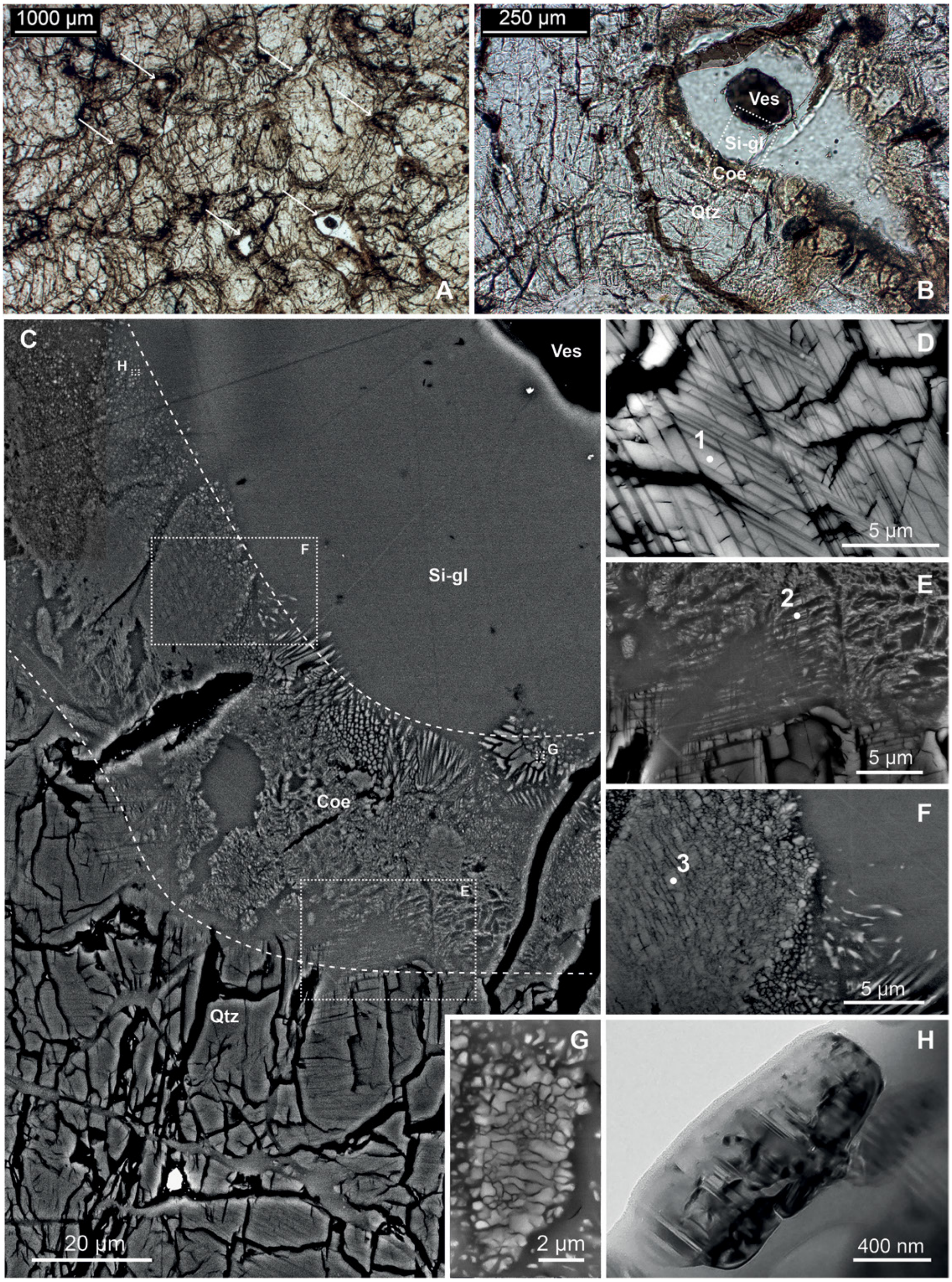

Figure 2. Symplectic regions in shocked sandstone (sample L23) from Kamil Crater, southwest Egypt. A: Optical micrograph showing symplectic regions (dark opaque regions with, in places, transparent colorless cores of vesicular silica glass; arrows) localized around intensely fractured quartz crystals. B: Optical micrograph of the symplectic region imaged in the following panels. Qtz—quartz, Coe—coesite, Si-gl—silica glass, Ves—vesicle. C: Mosaic of backscattered electron (BSE) images showing a representative section of the symplectic regions within shocked quartz grains. From bottom to top, the dashed lines limit the host "quartz zone" consisting of strongly shocked quartz grains bearing planar deformation features (PDFs), the "coesite zone" dominated by polycrystalline domains of microcrystalline coesite set in silica glass, and the vesiculated "silica glass zone". D: Angular-selective BSE image of a quartz grain (Raman spectra #1 in Fig. 3) with two sets of PDFs from the "quartz zone." E: BSE image of the transition between the quartz zone and the coesite zone. PDFs in quartz abutting silica glass in the coesite zone are progressively widened. Tartan-like polycrystalline domains within this transition domain consist of quartz-coesite intergrowths (Raman spectra #2 in Fig. 3) set in silica glass. Note the parallelism, despite some mobilization, between the orientations of the coesite-quartz intergrowths and the PDFs in quartz. F: BSE image of a polycrystalline domains of coesite in the coesite zone (Raman spectra #3 in Fig. 3) showing slightly mobilized planar arrangements of microcrystals along two directions at its core (left) and flame-like resorption textures at its rim (right). G: BSE image of polycrystalline coesite domain in silica glass showing resorption textures in the coesite zone. H: Bright-field transmission electron microscopy (TEM) image of an individual rounded coesite grain floating in silica glass showing (010) polysynthetic twinning in the coesite zone. Phase identification by energy-dispersive X-ray spectroscopy (EDS), Raman, and TEM analyses.

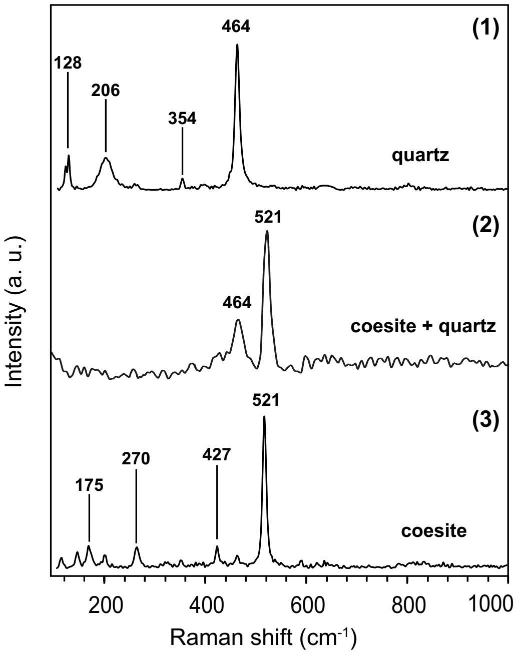

Figure 3. Raman spectra of silica phases in symplectic regions of shocked sandstone L23 from Kamil Crater, southwest Egypt. See Figure 2 for relative laser spot locations.

transmission electron microscopy (TEM). Details of the analytical procedures and additional data are given in the GSA Data Repository[1].

RESULTS

The shocked sandstone ejecta studied in this work is a pale, medium-grained quartzarenite (Figs. 2A and B) dominated by heavily shocked, equigranular quartz grains with an average grain size of 1 mm (~78 vol%) and including accessory tourmaline and zircon (Fazio et al. 2014). Intergranular veins and pockets (up to 1 mm across; ~22 vol%) of silica glass contain microcrystalline coesite (Figs. 2B and 2C). These domains are microstructurally analogous to the so-called symplectic regions first described in the Coconino Sandstones from the Barringer Crater (aka Meteor Crater), Arizona, USA (Kieffer et al., 1976).

Shock features in quartz include strong undulose extinction, multiple sets of planar fractures, and planar deformation features (PDFs) (Fig. 2D). The most frequent orientations of PDFs are $\{10\bar{1}3\}$, 23%, and $\{10\bar{1}2\}$, 14% (Fazio et al., 2014), indicating shock pressures of 20–25 GPa according to the calibration by Stöffler and Langenhorst (1994) for crystalline rocks. Consistently, a shock stage III, corresponding to ~20 GPa, is inferred from the amount of symplectic material, according to new shock calibration for porous quartz-bearing rocks by Kowitz et al. (2016), assuming a porosity of <~15 vol% in the target rocks, as identified by Fazio et al. (2014) at Kamil Crater.

Intergranular symplectic regions show microstructural zoning. From the core of the quartz crystals to the core of the symplectic regions, we distinguish a “quartz zone,” a “coesite zone,” and a “silica glass” zone (Fig. 2C). The quartz zone consists of shocked quartz, as described above (Fig. 2D). The coesite zone, up to several tens of microns in thickness, consists of polycrystalline aggregates of micro- to nano-crystalline (<5 µm) coesite set in pure silica glass; i.e., lechatelierite. The silica glass zone consists of homogeneous lechatelierite with usually one central bubble up to ~100 µm across.

In the coesite zone, coesite grains at the cores of individual aggregates are arranged along sets of planes and individually separated by silica glass (Figs. 2E–2G), causing mottled to tartan-like textures. In contrast, they are entrained in silica glass with flame-like resorption textures along their margins. Combined SEM and TEM observations indicate that coesite grains in individual mottled-tartan domains are uniformly oriented (Fig. 2F; see the Data Repository), supporting an origin from a common protolith crystal. Coesite shows fine (down to a few nanometers in thickness) polysynthetic twinning parallel to the (010) plane (Fig. 2H). Adjacent to the quartz zone, grains in tartan-like patterns consist of coesite plus quartz intergrowths arranged along planes that are nearly parallel to PDFs of the quartz grains in the adjacent quartz zone (Fig. 2E). Also, PDFs in the quartz zone abutting silica glass in the coesite zone are widened as a result of resorption (Fig. 2C).

Other shock features at the margins of quartz grains include incipient melts of intergranular tourmaline and baddeleyite (see Fazio et al., 2014, their figure 9B). The latter, likely the thermal product of zircon, indicates local temperatures in excess of ~1960 K (e.g., Timms et al., 2017). Fazio et al. (2014) also reported the occurrence of traces of stishovite in the same sandstone (L23) studied in this work, detected by X-ray powder diffraction. Despite careful search, we could not locate this high-pressure silica polymorph.

DISCUSSION

Petrographic data on shocked sandstones from Kamil Crater confirm that coesite in sedimentary rocks forms locally in symplectic regions, as reported in the literature from other impact structures (e.g., Kieffer et al., 1976). The resorption textures observed in the coesite zone, along with the melt-resorbed PDFs of the quartz crystals abutting the symplectic regions, suggest that interstitial silica glass (lechatelierite) formed by melting of coesite, coesite+quartz intergrowths, and PDF-bearing quartz crystals at temperatures above ~3000 K. The coesite-quartz intergrowths in the tartan-like aggregates indicate substitution of coesite at the expense of the PDF-bearing quartz crystals (Figs. 2E and 2F) through direct quartz-coesite subsolidus transformation. Such subsolidus transformation has been recently hypothesized for impact coesite in shock veins of meta-quartzites from the ~300-km-diameter Paleoproterozoic Vredefort impact structure (Spray and Boonsue, 2018). This mechanism is, however, in contrast with two current models for the formation of impact coesite at the ~24-km-diameter Ries (Germany) and the 1.8-km-diameter Xiuyan (China) impact craters, based on the microstructural observation of polycrystalline aggregates set in diaplectic silica glass of shocked, non-porous clasts in suevite. These models envisage coesite formation during shock unloading (i.e., when the pressure release path passes through the coesite stability field) through crystallization from a silica shock melt (Langenhorst, 2003; Chen et al., 2010; Fazio et al., 2017) or subsolidus nucleation from highly densified diaplectic silica glass (Stähle et al., 2008). Neither of the two nucleation processes can explain the localized occurrence of coesite at the margins of the symplectic regions in our sample. This suggests that the mechanism of coesite formation in porous target rocks may differ from that in crystalline target rocks.

The equilibrium pressure conditions for coesite formation, 3–10 GPa, are significantly lower than the ~20 GPa required to explain the amount of symplectic material and PDF orientations in the shocked quartz of the studied rock. This implies significant heterogeneity in the space-time distribution of pressure-temperature conditions within the rock. Heterogeneous and asynchronous distribution of peak pressures and temperatures is known to occur in porous rocks due to pore collapse induced by the passage of shock waves. We thus discuss the shock features in our sample within the context of the recent numerical simulation of shock-induced pore collapse by Güldemeister et al. (2013), as schematically represented in Figure 4. The passage of a shock wave generated by a moderate shock event (e.g., ~20 GPa) in a quartz+pore system produces PDFs in the quartz zone (Fig. 4A) and causes the collapse of pores. Pore collapse induces localized decompression, followed by pressure amplification in adjacent quartz crystals. This leads first to the subsolidus transformation of quartz into a high-pressure silica polymorph (coesite in the present case), which

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[1] GSA Data Repository item 2018269, analytical methods and Figure DR1, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.

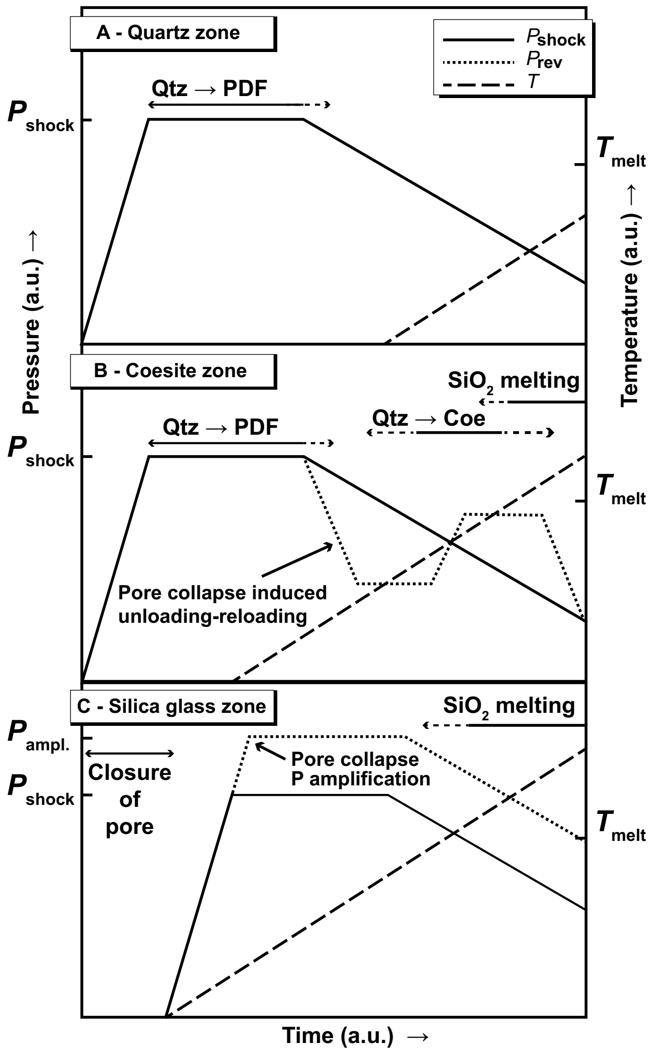

Figure 4. Schematic variation of pressure (*P*; solid and dotted lines for shock pressure and pressure amplification [ampl.] due to pore collapse, respectively) and temperature (*T*; dashed line) during the passage of a shock wave in a quartz+pore system, qualitatively extrapolated from numerical simulations on shock-wave propagation in porous media by Güldemeister et al. (2013). Panels show different domains of the quartz+pore system, represented by the "quartz", "coesite", and "silica glass" zones in Figure 1. Occurrence of silica phase transformations are shown. P_{shock}—shock pressure; P_{rev}—pressure associated with shock wave reverberation; T_{melt}—silica melting temperature; a.u.—arbitrary units. See text for explanation.

subsequently melts when temperatures increase due to frictional heating induced by grain compaction (Fig. 4B). Pressure amplification and frictional heating are greatest at the center of the collapsed pore (Fig. 4C), causing complete melting of the high-pressure silica polymorphs (coesite in the present case) formed earlier during the decompression–initial pressure amplification stage. The preferential melting of coesite relative to quartz could be due to its metastability at ambient pressure and the smaller grain size (higher surface/volume ratio). Note that the temperature and pressure reported in Figure 4 are only qualitative estimates, and that the foremost parameter determining the formation and growth of coesite is the time spent within its stability field. Shock-front reverberation caused by the presence of pores and discontinuities in the shocked material could last long enough (milliseconds, according to Güldemeister et al. [2013]) to allow the transformation of quartz into coesite. This transformation may be energetically and topologically facilitated by the development of pervasive twinning in shocked coesite. Although we observed no stishovite (Fazio et al., 2014), it may have been present as relic crystals originally produced near the core of the symplectic regions and then melted away, similar to coesite.

Mineralogical and petrographic data from shocked Kamil Crater sandstones thus document the effective role of pore collapse in producing heterogeneous pressure-temperature-time (*P-T-t*) distributions in porous targets, as predicted by numerical models in the literature. This is relevant in defining the *P-T-t* paths of shock metamorphic rocks (porous versus crystalline), and therefore the shock classification of impactites and impact scenarios (e.g., Kowitz et al. 2016). The mechanism of coesite formation proposed in this study should apply to all moderately shocked, quartz-bearing sedimentary targets, including those at Barringer and Haughton (Nunavut, Canada) craters.

ACKNOWLEDGMENTS

This work was supported by the Ministero dell'Istruzione dell'Università e della Ricerca (PI# 20177X22NL). The manuscript benefited from the constructive criticism of three anonymous reviewers and editor Chris Clark..

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Manuscript received 7 May 2018
Revised manuscript received 29 June 2018
Manuscript accepted 6 July 2018

Printed in USA