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Geochimica et Cosmochimica Acta 120 (2013) 263–279

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Sulfur degassing due to contact metamorphism during flood basalt eruptions

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Received 16 November 2012; accepted in revised form 20 June 2013; available online 2 July 2013

Abstract

We present a study aimed at quantifying the potential for generating sulfur-rich gas emissions from the devolatilization of sediments accompanying sill emplacement during flood basalt eruptions. The potential contribution of sulfur-rich gases from sediments might augment substantially the magma-derived sulfur gases and hence impact regional and global climate. We demonstrate, from a detailed outcrop-scale study, that sulfur and total organic carbon have been devolatilized from shales immediately surrounding a 3-m thick dolerite sill on the Isle of Skye, Scotland. Localized partial melting occurred within a few centimetres of the contact in the shale, generating melt-filled cracks. Pyrite decomposed on heating within 80 cm of the contact, generating sulfur-rich gases (a mixture of H_2S and SO_2) and pyrrhotite. The pyrrhotite shows ^{32}S enrichment, due to loss of ^{34}S-enriched SO_2. Further decomposition and oxidation of pyrrhotite resulted in hematite and/or magnetite within a few cm of the contact. Iron sulfates were produced during retrogressive cooling and oxidation within 20 cm of the contact. Decarbonation of the sediments due to heating is also observed, particularly along the upper contact of the sill, where increasing $\delta^{13}C$ is consistent with loss of methane gas. The geochemical and mineralogical features observed in the shales are consistent with a short-lived intrusion, emplaced in <5 h. The dolerite magma contains pervasive pyrite and localized sulfur concentrations greater than the sulfur concentration at sulfide liquid saturation, consistent with addition of sulfur (perhaps from sediments) at a late stage. Our study provides evidence for desulfurization, as well as decarbonation, of shales adjacent to an igneous intrusion. The liberated fluids, rich in sulfur and carbon, are likely to be focused along regions of low pore fluid pressure along the margins of the sill. The sulfur gases liberated from the sediments would have augmented the sulfur dioxide (and hydrogen sulfide) yield of the eruption substantially, had they reached the surface. This enhancement of the magmatic sulfur budget has important implications for the climate impact of large flood basalt eruptions that erupt through thick, volatile-rich sedimentary sequences.

1. INTRODUCTION

This study is aimed at quantifying the mechanism of assimilation of sedimentary sulfur into magmas in large igneous provinces, and how it might augment the total sulfur yield of the eruptions, and hence impact climate. Whilst there have been many studies of desulfurization of sediments in regional metamorphic terrains (e.g. Tomkins, 2010), there are few focused on the effect of heating and partial melting of sediments by intruding magmas.

The emplacement of some Large Igneous Provinces (LIPs) is temporally coincident with biological mass extinction in the geological record, although the cause of this synchronicity remains enigmatic (Wignall, 2001; Courtillot and Renne, 2003; Svenson et al., 2004; Saunders and Reichow, 2009; Ganino and Arndt, 2012). The leading explanation for the coincidence between LIPs and mass extinction is the possible climate change caused by volcanic emissions

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http://dx.doi.org/10.1016/j.gca.2013.06.025

during the emplacement of the LIP (Wignall, 2001). Large Igneous Provinces are the result of bursts of intraplate volcanism of short duration (<5 Ma) and large volume (>1×10^6 km^3), which includes both continental flood basalts and oceanic plateaus (Bryan and Ernst, 2008). The critical factor determining the possible climatic impact during LIP emplacement may be the type of rock into which the magmas are intruded into and/or erupted through (Svenson et al., 2004, 2006, 2009; Aarnes et al., 2010a,b, 2011; Ganino and Arndt, 2012). Of the four large igneous provinces associated with major mass extinctions (Siberian Traps, Deccan Traps, Central Atlantic Magmatic Province and Emeishan), three are emplaced into volatile-rich country rocks, comprising evaporites, dolomites, coals and oil shales (Ganino and Arndt, 2012). The hypothesis is that these oil shales and evaporites decompose on heating, generating excess carbon and sulfur-rich gases, which can cause environmental degradation due to climate change (Svenson et al., 2009).

Large emissions of gases from the solid earth, magmatic or otherwise, impact the climate in dramatic yet complex ways. Carbon dioxide is a greenhouse gas with potential to cause global warming. The relatively low CO_2 content of the tholeiitic basalts erupted during LIP emplacement has been postulated to be insufficient to cause anything but modest warming (Caldeira and Rampino, 1990; Self et al., 2006). Heating of volatile-rich sediments by contact metamorphism will produce excess carbon (carbon dioxide, CO_2, carbon monoxide, CO and methane, CH_4) and halocarbon gases (Svenson et al., 2004, 2009; Aarnes et al., 2010a, 2011). Negative carbon isotope perturbations that often accompany emplacement of large igneous provinces require the input of a large mass of isotopically light carbon into Earth's surface environment (Wignall, 2001), consistent with organic carbon or methane outgassing from sediments (Svenson et al., 2004; Saunders and Reichow, 2009; Aarnes et al., 2011). Additionally, there is strong physical evidence for the devolatilization of sediments accompanying LIP eruptions in the form of gas pipe structures (Svenson et al., 2009). Geochemical evidence for devolatilization has focussed on laboratory studies of soil shale and evaporite decomposition (Svenson et al., 2009), and decarbonation reactions occurring in the thermal aureoles of sills (Aarnes et al., 2010a,b, 2011). These studies have allowed estimates of methane and CO_2 fluxes, which show that this mechanism is capable of producing the carbon isotope perturbations observed synchronous with LIP events (Retallack and Krill, 2006). The effect of large and prolonged emissions of CO_2 into the atmosphere may induce warming over long timescales (10^5–10^6 years; Dessert et al., 2003) as well as acidification of aqueous environments.

Sulfur dioxide (SO_2) injected into the lower stratosphere during volcanic eruptions reacts with hydroxyl radicals to form sulfate aerosol (Robock, 2000). The aerosol scatters incoming visible and UV radiation from the sun, and absorbs infrared radiation. Interaction between sulfate aerosols and solar insolation produces stratospheric heating and tropospheric (and Earth surface) cooling. The net effect is that the total flux of radiation reaching the Earth's surface may be drastically reduced (Robock, 2000). For large eruptions (with a Volcanic Explosivity Index, or VEI of >7) a cooling of up to 10 °C may persist up to a decade after the cessation of volcanic activity (Rampino and Self, 1992; Robock, 2000). It is thought that for eruptions of this size, the fraction of transmitted sunlight might be reduced to <10%, which greatly impacts the rate of photosynthesis. Aerosol mass loadings of >3000 Mt, which within the range estimated for the Roza Member of the Colombia River Flood Basalt eruptions, might have led to only 1% of sunlight reaching the Earth's surface, under which conditions photosynthesis would cease (Self et al., 2006). For eruptions where volcanic activity is maintained, with pauses equal to or less than the residence time of aerosol, the climate impact can be prolonged for the duration of the volcanic activity and the resulting cooling may be larger (Rampino and Self, 1982). The implications of such prolonged cooling and reduced radiative flux could be catastrophic for life on Earth, primarily through the shortening of the growing season and the inhibition of photosynthesis, eventually leading to extensive vegetation die-off. It is likely that cooling due to sulfate aerosol may have been prolonged for periods of frequent eruptions (every few years) and so a scenario of sulfate-induced cooling over 10^3–10^4 years might be envisaged in principle. The relatively short-lived sulfate-induced cooling during eruptions is unlikely to be preserved in the geological record, yet the impact of SO_2 emissions might be of crucial importance in evaluating the causes of mass extinctions (Li et al., 2012). Furthermore the native sulfur content of most theoliitic basalts is too low to cause the massive global catastrophes associated with some LIPs, and the incorporation of sulfur from sediments into lava is poorly understood.

Isotopic studies of the sulfur budget of the ore-bearing sills and non-mineralised lava flows in the Norilsk region of the Siberian Traps, associated with the Permo-Triassic mass extinction, have led to hypotheses of sulfur assimilation from the sediments to explain the heavy isotope signature of the magmatic sulfur (Ripley and Li, 2003; Grinenko, 1985). Recent studies of komatiite-hosted ore deposits have presented evidence from sulfur isotopes for assimilation of hydrothermal (Bekker et al., 2009) and crustal (Fiorentini et al., 2012a, b) sulfur. These studies offer promise for the use of sulfur isotopes to understand the assimilation of sulfur volatiles into igneous eruptions. There have been, however, few studies on the behaviour of sulfur during contact metamorphism on a local scale that might allow us to estimate the potential impact of assimilation of sedimentary sulfur on the total sulfur budget of LIPs. In particular, the relative importance of volatile assimilation into magmas and degassing during eruption (necessary to explain the sulfur isotope composition), and sediment devolatilization and direct outgassing to the atmosphere (as has been proposed for C-rich gases in such settings, e.g. Svenson et al., 2009) is not clear. In order to address these questions, we must elucidate the mechanism by which sulfur is liberated during contact metamorphism, and make estimates of the potential sulfur yield with varying intrusion parameters. Sulfur isotopes are fractionated during devolatilization reactions, and also during degassing from partial melts, making them a potentially valuable tool in deciphering these processes.

In this paper, we use a detailed, outcrop-scale approach to investigate the progressive changes in both bulk sulfur