

# Cratonization, a cause for the rise of atmospheric oxygen and ocean sulphate in early Proterozoic time

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The enlarged land mass during the late Archaean resulted in the initiation of significant subaerial igneous activity. This caused an increased flux of SO<sub>2</sub> gas and SO<sub>4</sub><sup>2-</sup> into the surface environments, which unbalanced the steady-state redox conditions of Archaean and led to the global oxidation in early Proterozoic time. During the transition period, the concentration of marine sulphate progressively increased by incorporating hydrated SO<sub>2</sub> gas ( $\delta^{34}\text{S} < +6\%$ ) and eroded magmatic-hydrothermal sulphates ( $\delta^{34}\text{S} < +8\%$ ). Fixation of S as sulphides in sediments was accompanied by a small isotopic fractionation in the ocean of low sulphate concentration. This is supported by generally positive  $\delta^{34}\text{S}$  for sedimentary sulphides of late Archaean and early Proterozoic time.

## Introduction

It is broadly accepted that surface conditions on Earth during the Archaean presented a reduced environment. Profound changes in the surface environment, extensive glaciation and oxygenation, took place during early Proterozoic time. Steady-state reduced condition in Archaean was disturbed during late Archaean-early Proterozoic time either by increased oxidizing fluxes or decreased reducing fluxes to the surface environments. The latter has been considered to be the cause as magma production declined in response to declining radioactive heat generation. This,

however, cannot account for the rapid change during early Proterozoic time. Furthermore, this model would imply progressive oxidation of Earth's surface without steady-state conditions. Here, I suggest that the increased land size in late Archaean resulted in an increased subaerial igneous activity and an imbalance in global redox conditions.

## Sulphur originated from magmas

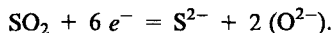
Recent eruptions at Mt. Pinatubo, Philippines, and El Chichón, Mexico, highlighted the significance of volcanic SO<sub>2</sub> emission. The presence of anhydrite phenocrysts in the eruption products demonstrates that large amounts of oxidized S species are released to the surface environment in addition to SO<sub>2</sub> gas alone. The estimates of total annual volcanic SO<sub>2</sub> gas made by various researchers since 1980 range from 13 to 50 Mt/yr (Bluth *et al*, 1993). In addition, significant SO<sub>2</sub> is adsorbed on ash and much of S released from silicate magma are converted into SO<sub>4</sub><sup>2-</sup> by hydrolysis reactions before reaching the surface. Total oxidizing sulphur species discharged by global igneous activity is estimated to be 22 to 29 Mt/yr equiv. SO<sub>2</sub> (Table 1) using the data from recent eruptions. Combined with the SO<sub>2</sub> gas, total ranging from 25 to 53 Mt/yr of SO<sub>2</sub> equiv. is discharged to the surface environments. The estimate is comparable to the estimate based on global magma production rate by Crisp (1984).

Submarine magmas normally retain S (~1,500 ppm) as S<sup>2-</sup> and HS<sup>-</sup> within the melts due to hydrostatic pressures. After solidification, sulphide S retained in volcanic rocks is eroded and eventually fixed as sulphides in sediments. All processes in the surface environment are not accompanied by valency changes of S and the S derived from submarine igneous rocks has no impact on the surface redox conditions. Subaerial magmas, on the other hand, release most of S as SO<sub>2</sub> into the atmosphere and retain little S, < 50 ppm. Some SO<sub>2</sub> released from magmas may be adsorbed on ash during eruption, and some are converted to SO<sub>4</sub><sup>2-</sup> before reaching the surface. These S species are eroded into the ocean and are

TABLE 1. SO<sub>2</sub> discharged from subaerial volcanoes in Mt (10<sup>12</sup> g)

	SO <sub>2</sub> gas	SO <sub>4</sub> <sup>2-</sup> (SO <sub>2</sub> equiv)
Erupting volcanoes	4-12	
subsurface consumption		4-12
adsorbed on ash		1 - 3
Non-erupting volcanoes	7-14.2	
subsurface consumption		7-14
Sub-total	13-24	12-29
Grand total		25-53

eventually fixed as sulphides in sediments. The net effect of S originated from subaerial magmas to the surface environments is oxidation:



#### Change of sulphur species released from magmas

Late Archaean is characterized by accretion and cratonization. Areal exposure of land increased during that period, as shown by a sharp increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  of ocean carbonates (Veizer *et al*, 1982). This was also a change in the style of igneous activity. Igneous rocks confined only to the continental environment, such as extensive dyke swarms, large layered intrusions and alkaline igneous rocks, started to appear only in late Archaean time. Subaerial volcanic rocks became significant during the late Archaean time, which is in contrast with exclusively submarine volcanic rocks of early Archaean age. Hot-spot related subaerial magmatism probably occurred more often than before on the newly formed continental crust.

This transition during the late Archaean caused the increase in the ratio of (oxidized S)/(reduced S) released from magmas. The appearance of alkaline igneous rocks also contributed to the increased emission of  $\text{SO}_2$  gas and release of  $\text{SO}_4^{2-}$  to the

global surface environments as alkaline magmas are generally high in S.  $\text{SO}_2$  gas released from magmas have positive  $\delta^{34}\text{S}$ , < 6‰.  $\text{SO}_4^{2-}$  formed during magmatic-hydrothermal activity is also enriched in  $^{34}\text{S}$ , 8 to 10‰. Sedimentary sulphides formed from such sulphate of low concentrations would be also enriched in  $^{34}\text{S}$ . Positive  $\delta^{34}\text{S}$  values for sedimentary sulphides in late Archaean to early Proterozoic time (e.g., Skyring & Donnelly, 1982; Strauss, 1993) support the proposed opinion. High contents of volatile metals, such as Hg and As, in sedimentary rocks during that period (Cameron & Jonasson, 1972) are also consistent with the proposed model.

#### References

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