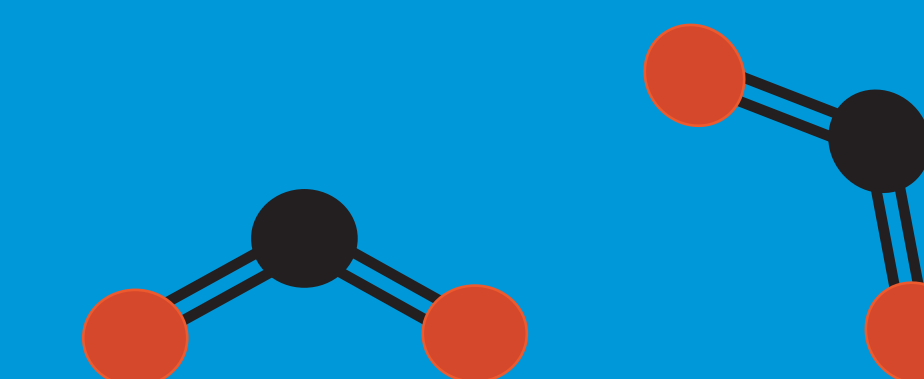
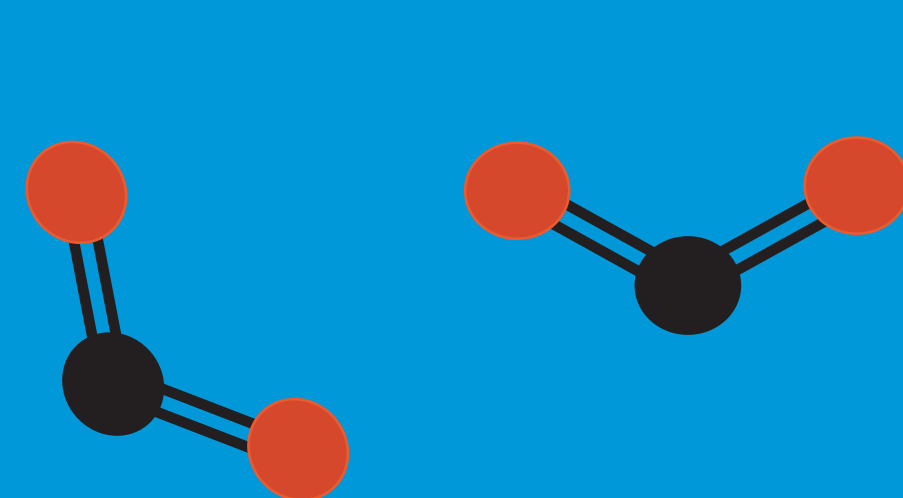




Anomalous Fractionation Patterns of Multiple-S-Isotopes in the Broadband UV Photolysis of He-SO₂

Andrew L. Masterson Advisors: Boswell A. Wing and James Farquhar
GEOL394H



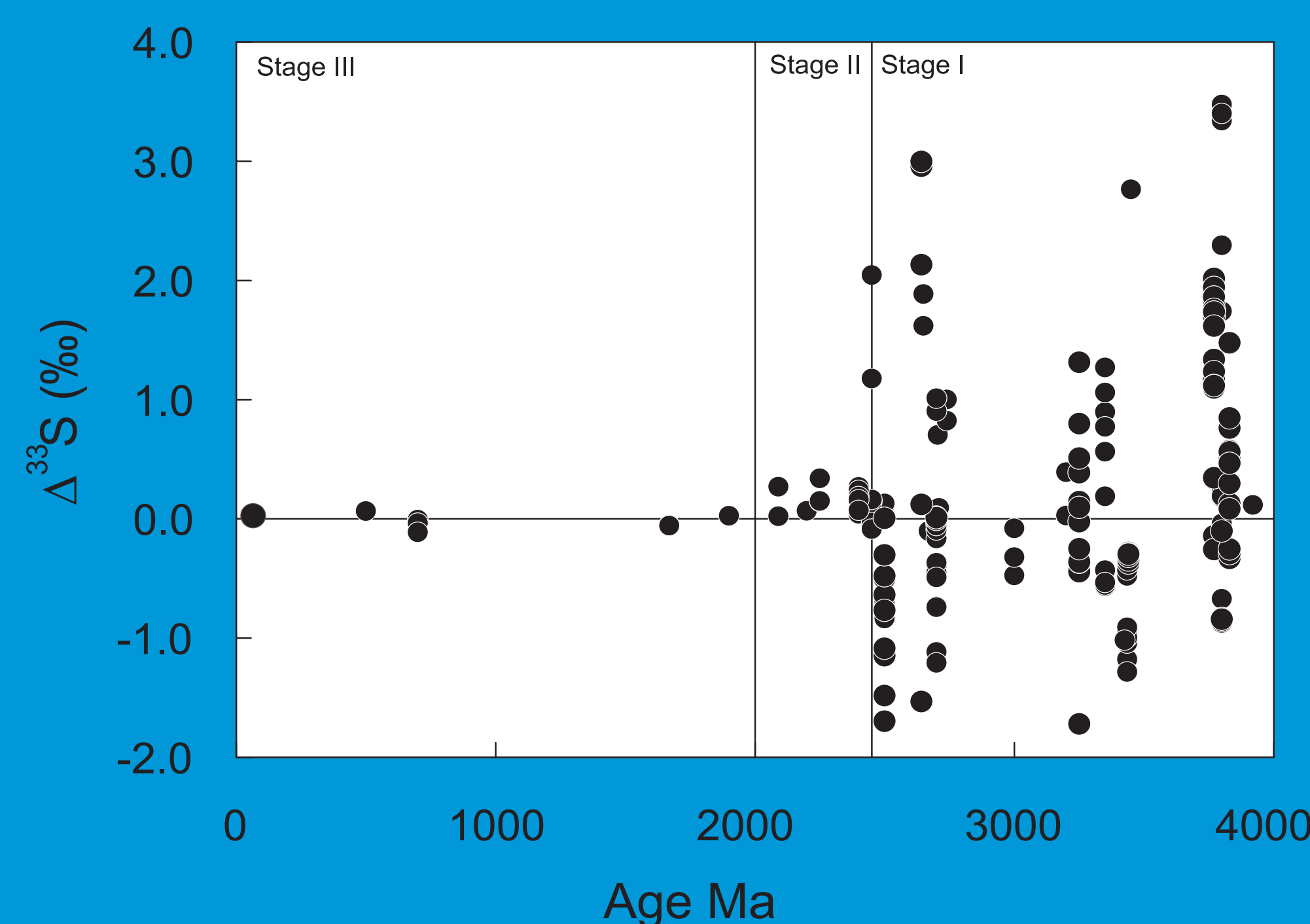
Introduction

Anomalous fractionation of multiple S isotopes present in Archean sulfides and sulfates

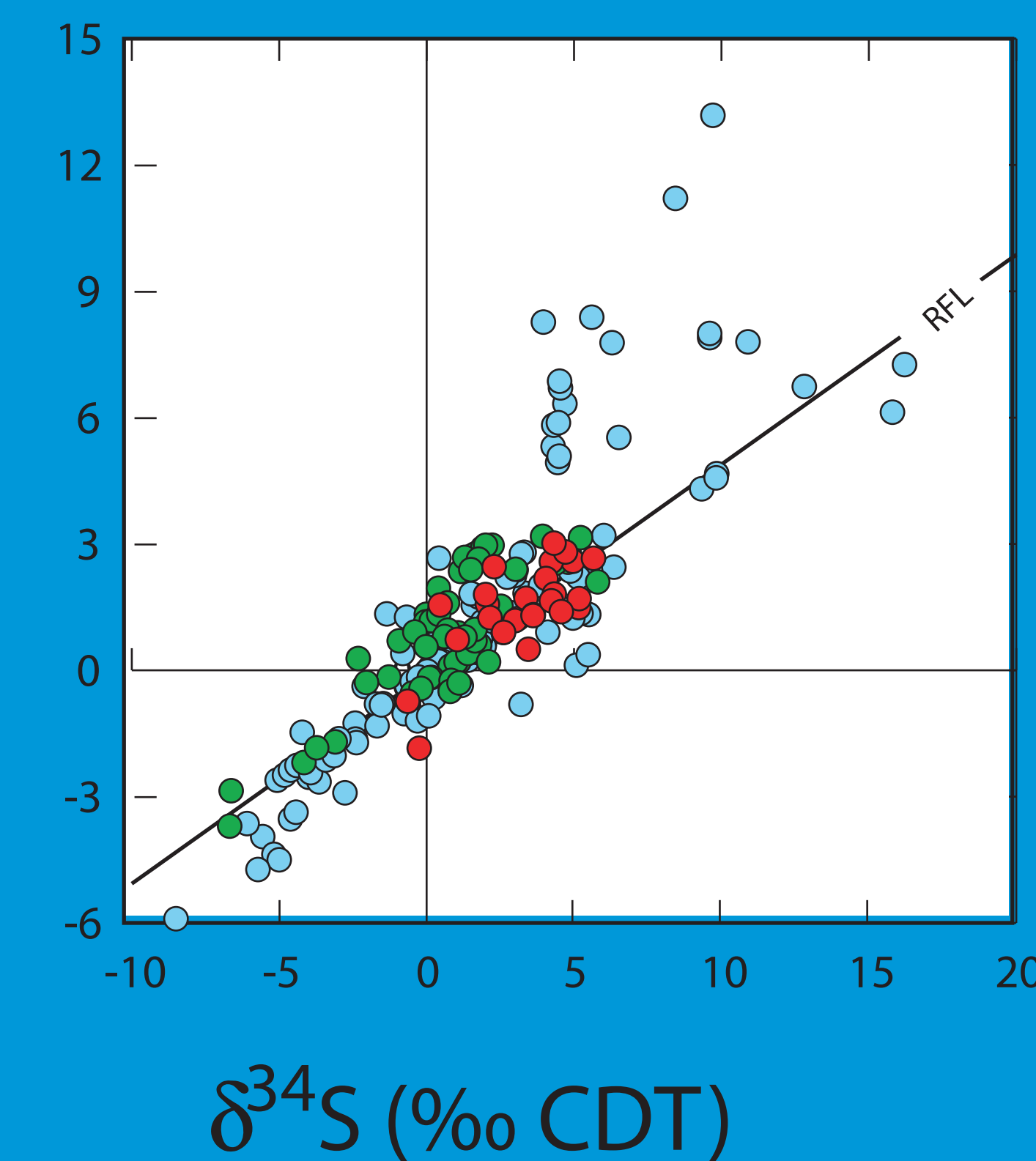
Associated with UV photochemical reactions of S-bearing gases

Anomalous fractionations used as oxygen paleobarometer

Patterns of anomalous fractionation ($\delta^{33}\text{S}/\delta^{34}\text{S}$, $\delta^{36}\text{S}/\delta^{34}\text{S}$, $\Delta^{36}\text{S}/\Delta^{33}\text{S}$) appear to vary across the UV-spectrum

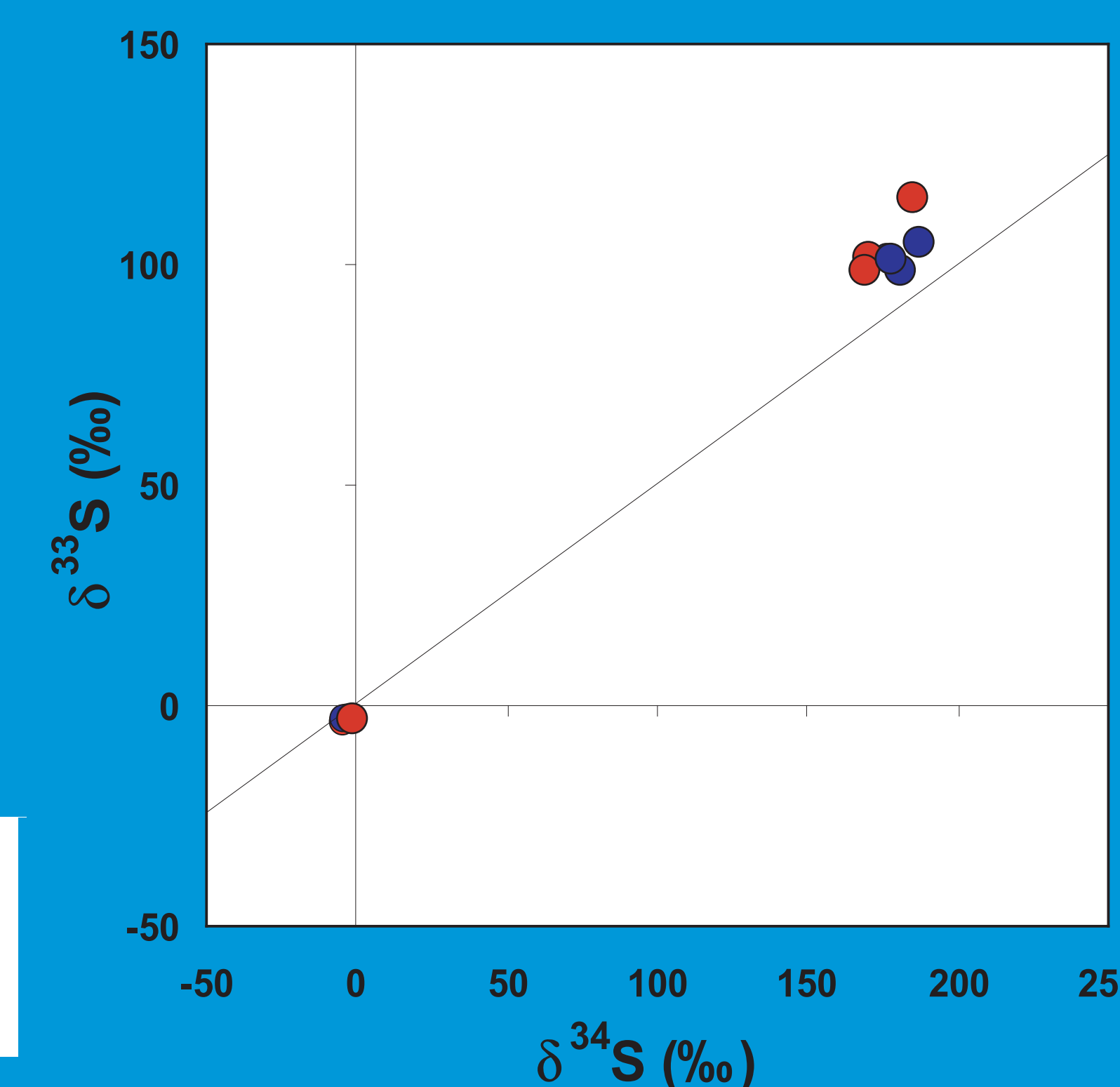


$\delta^{33}\text{S}$ (‰ CDT)

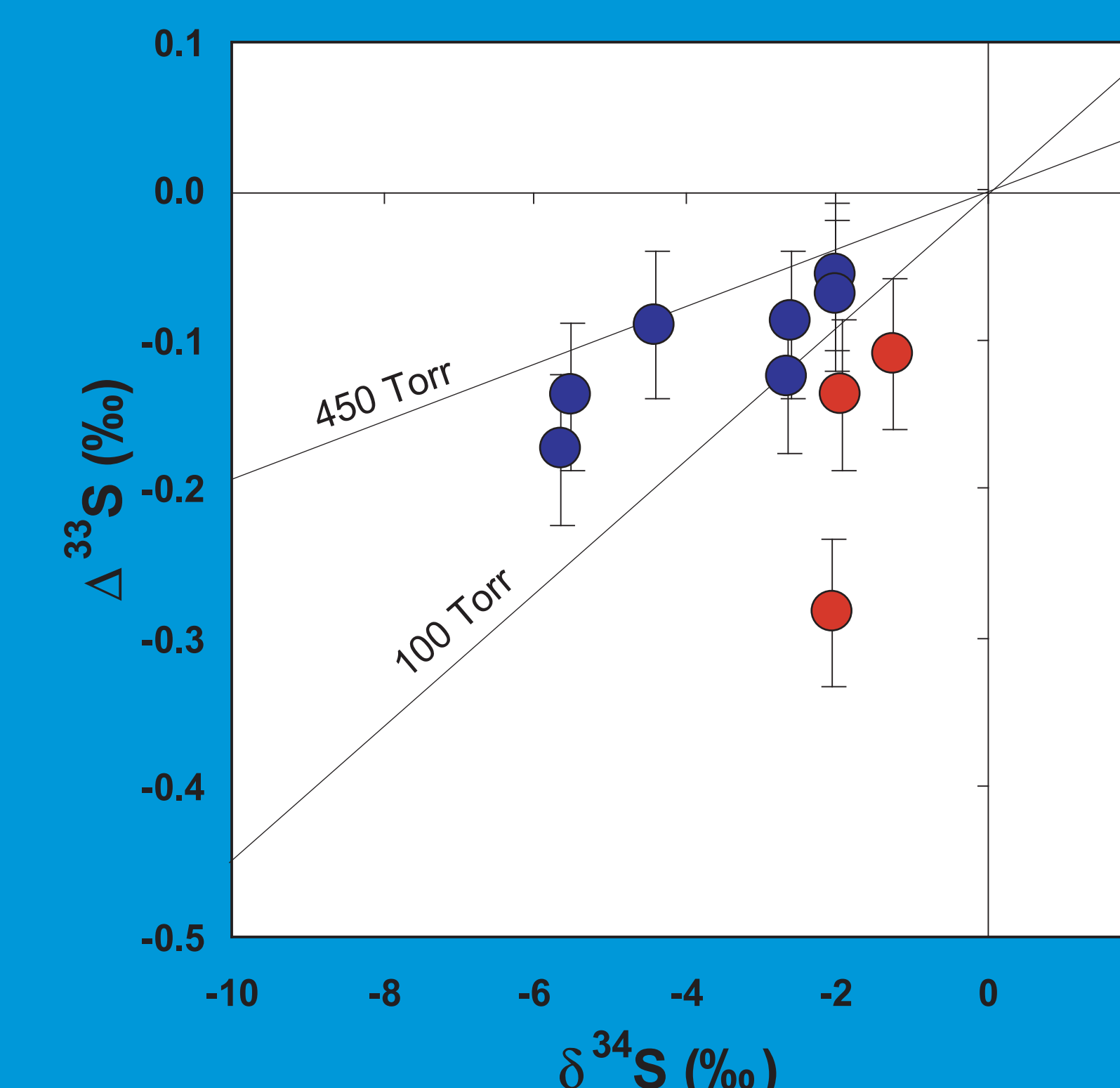


Sulfides and Sulfates
● >2450 Ma to <3000 Ma ● >3000 Ma to <3500 Ma ● >3500 Ma

Pure SO ₂	Elemental S	
$\delta^{33}\text{S}$ (±0.05‰) 114.53	$\delta^{33}\text{S}$ (±0.05‰) 185.92	$\delta^{33}\text{S}$ (±0.2‰) 336.2
$\delta^{34}\text{S}$ (±0.05‰) 98.78	$\delta^{34}\text{S}$ (±0.05‰) 170.09	$\delta^{34}\text{S}$ (±0.2‰) 310.5
$\Delta^{33}\text{S}$ (±0.05‰) -2.0	$\Delta^{33}\text{S}$ (±0.05‰) -2.3	$\Delta^{33}\text{S}$ (±0.2‰) -2.4



He-SO ₂	Elemental S	
pHe (Torr) 115	$\delta^{33}\text{S}$ (±0.05‰) 101.44	$\delta^{33}\text{S}$ (±0.2‰) 176.98
$\delta^{34}\text{S}$ (±0.05‰) 104.90	$\delta^{34}\text{S}$ (±0.05‰) 187.55	$\delta^{34}\text{S}$ (±0.2‰) 348.7
$\Delta^{33}\text{S}$ (±0.05‰) -2.9	$\Delta^{33}\text{S}$ (±0.05‰) -3.0	$\Delta^{33}\text{S}$ (±0.2‰) -3.8



Experimental SO₂ UV-photochemistry

Broadband (180-400 nm) irradiation produces elemental S with large anomalous fractionation

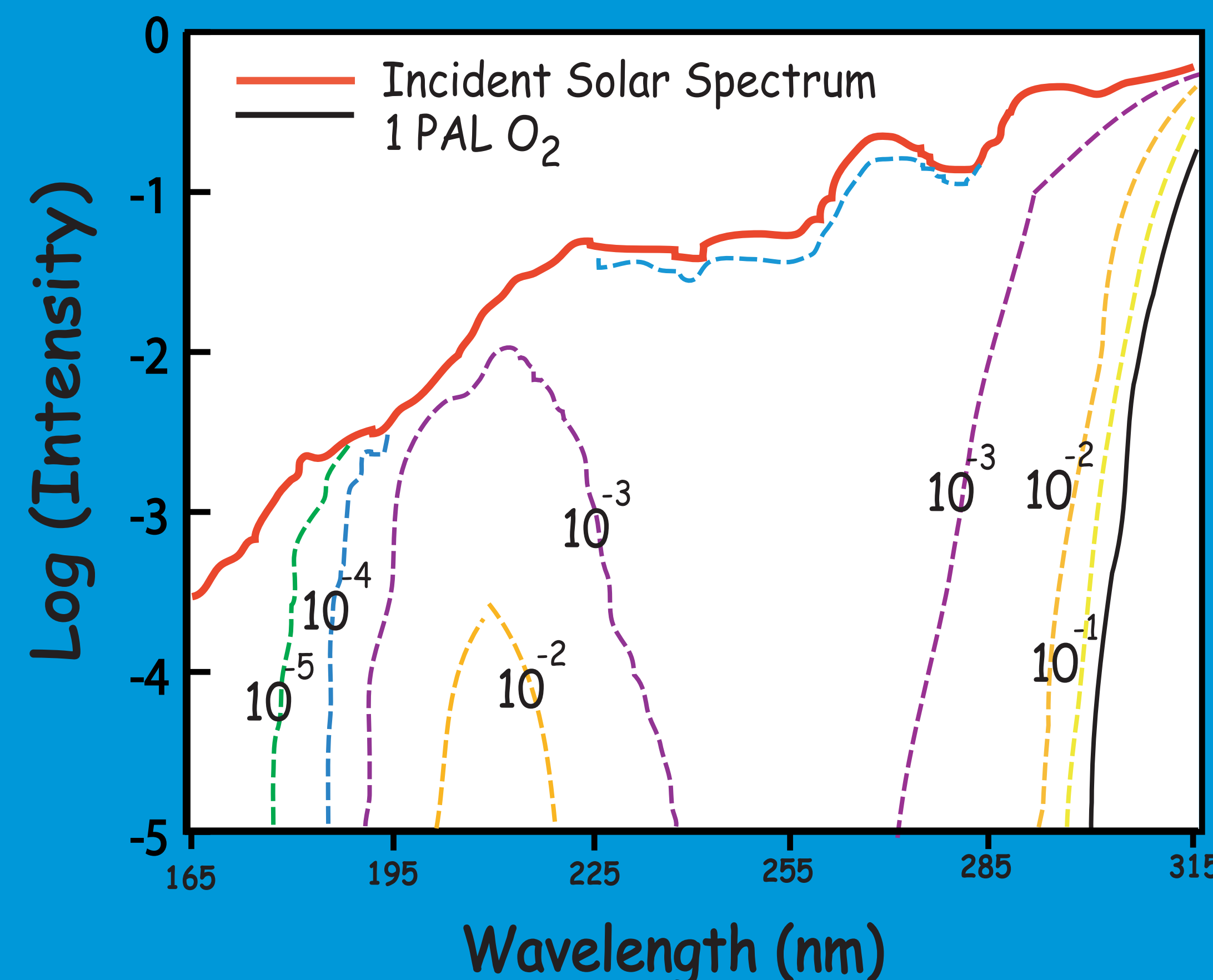
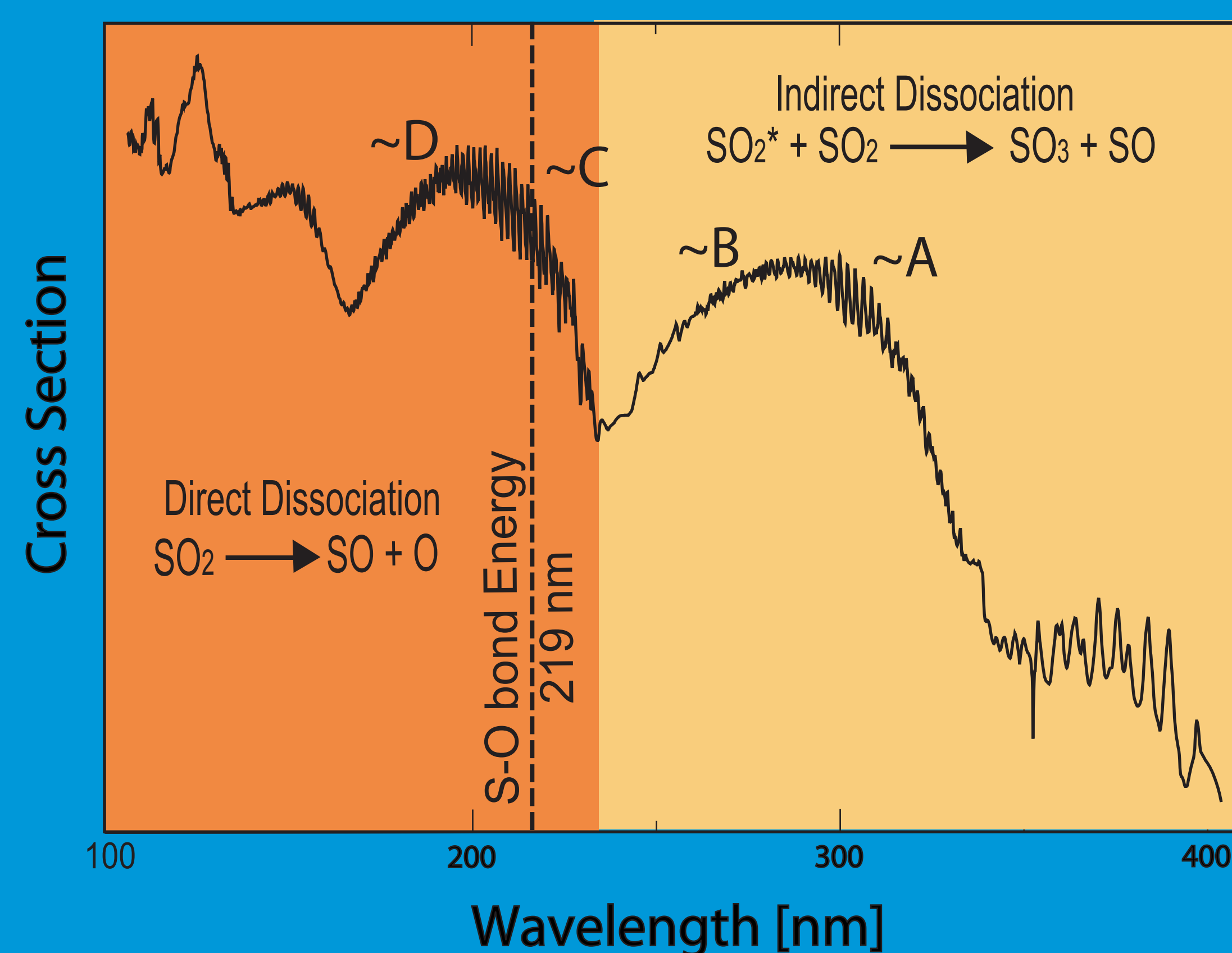
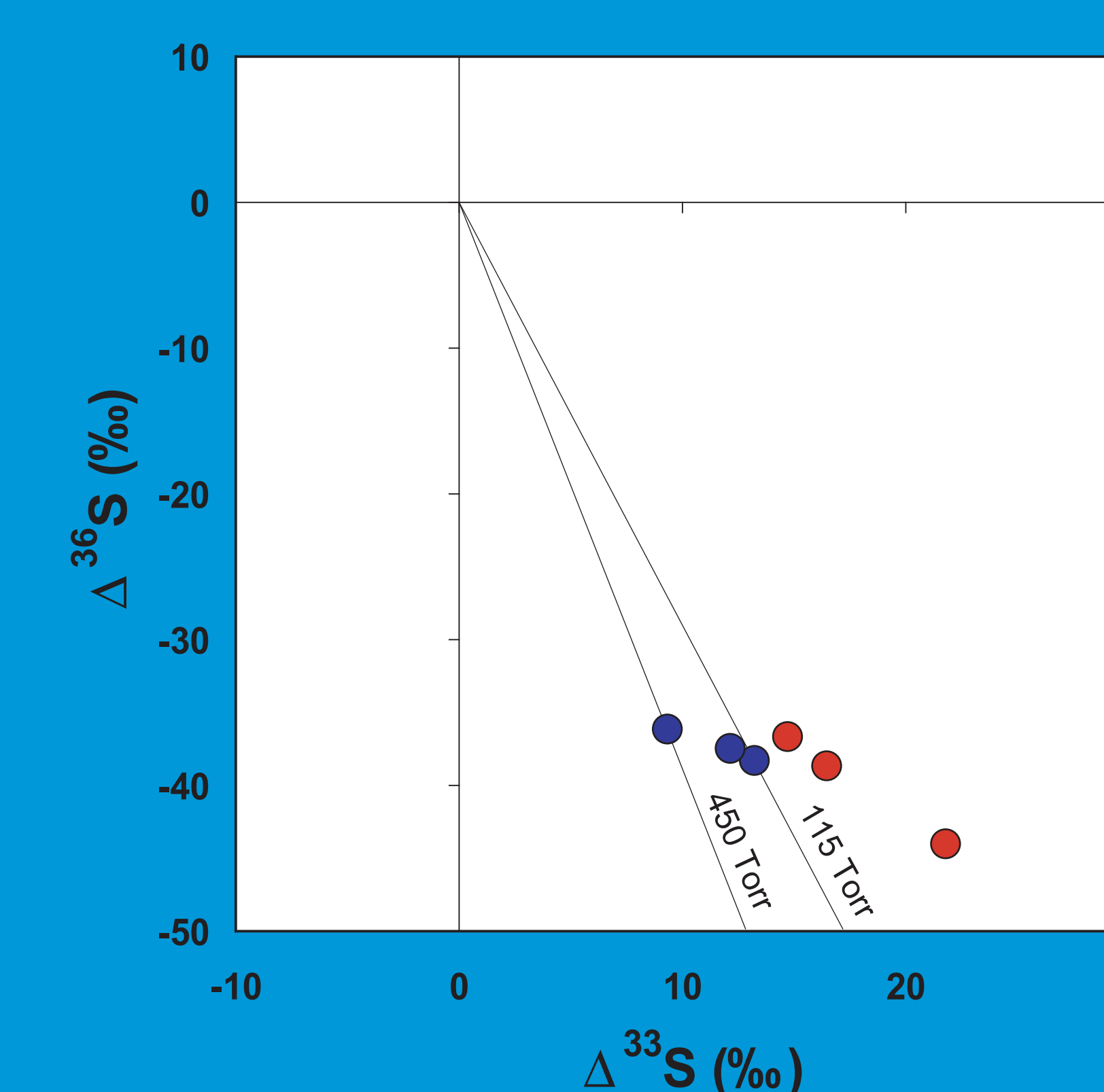
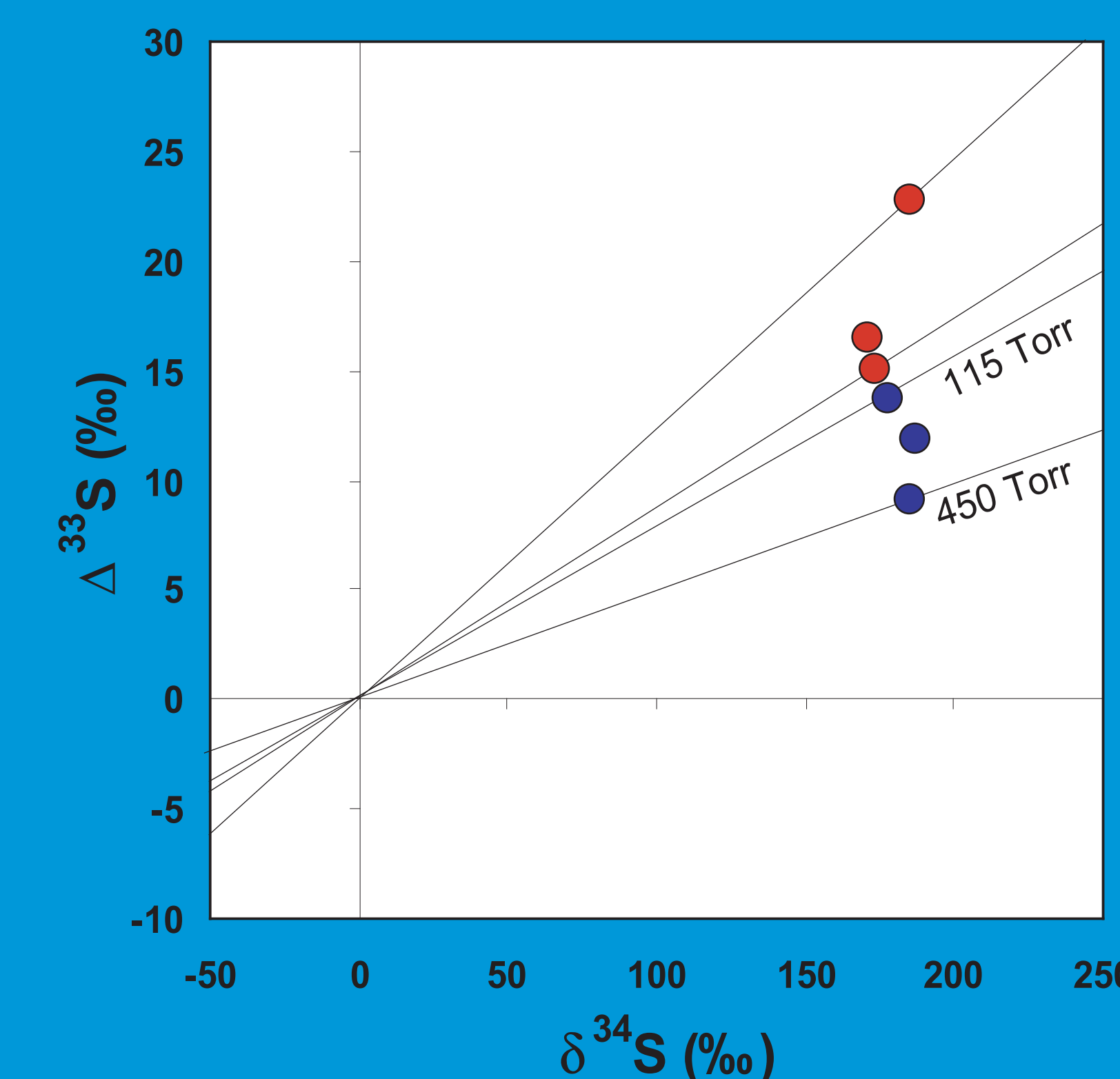
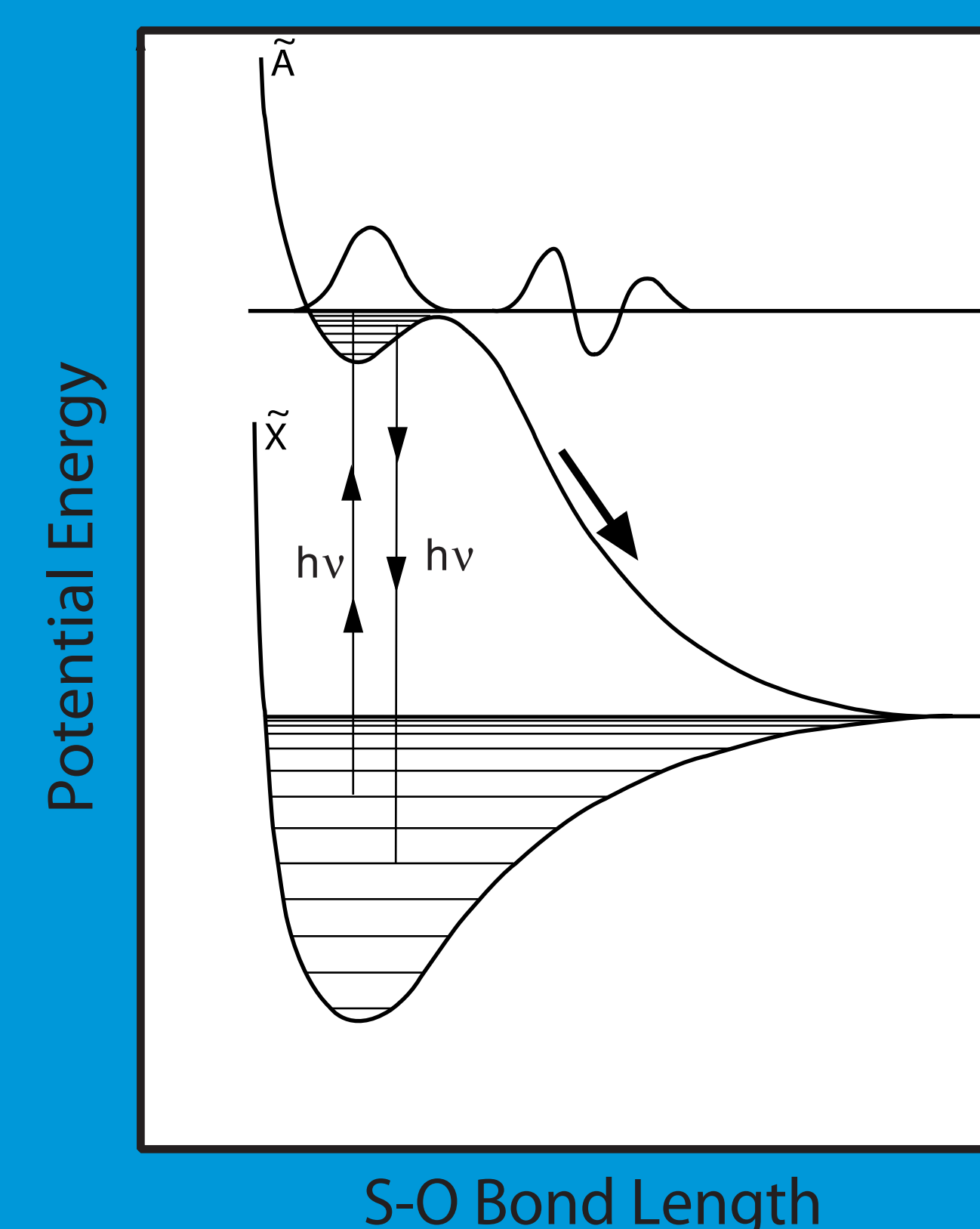
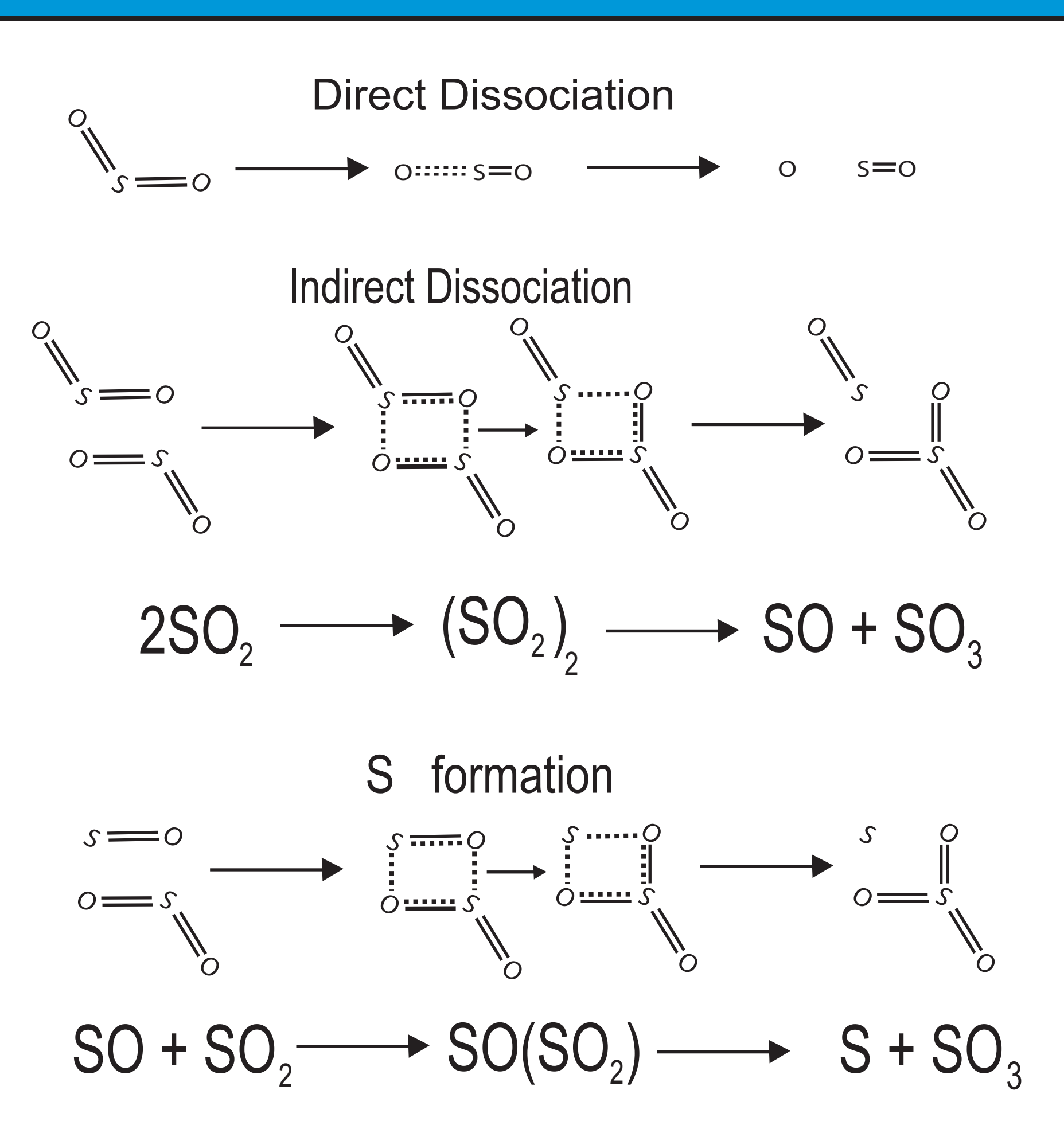
$$\delta^{33}\text{S}/\delta^{34}\text{S} \sim 0.6$$

$$\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -2$$

$$\delta^{34}\text{S} \sim 150-200 \text{ (‰)}$$

SO₂ Photolysis a combination of direct (SO₂ → SO + O) and indirect (SO₂* + SO₂ → SO₃ + SO) Dissociation

Fractionation Patterns of Direct and Indirect dissociation unknown



Inclusion of He decreases magnitude of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$

He ~450 Torr photolysis produces $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -4$

High pressures of He may interfere with SO → S + O

More negative $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ may indicate contribution from direct dissociation

Natural Solar UV-flux favors longer wavelengths, in contrast to laboratory photolysis

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