

**CARBOXYLIC ACIDS, SULFATES, AND
ORGANOSULFATES IN PROCESSED
CONTINENTAL ORGANIC AEROSOL OVER
THE SOUTHEAST PACIFIC OCEAN
DURING VOCALS-REX 2008**

**LELIA HAWKINS¹, L.M. Russell¹,
D.S. Covert², P.K. Quinn³, and T.S. Bates³**

¹Scripps Institution of Oceanography, UCSD

²Dept. of Atmospheric Sciences, Univ. of Washington

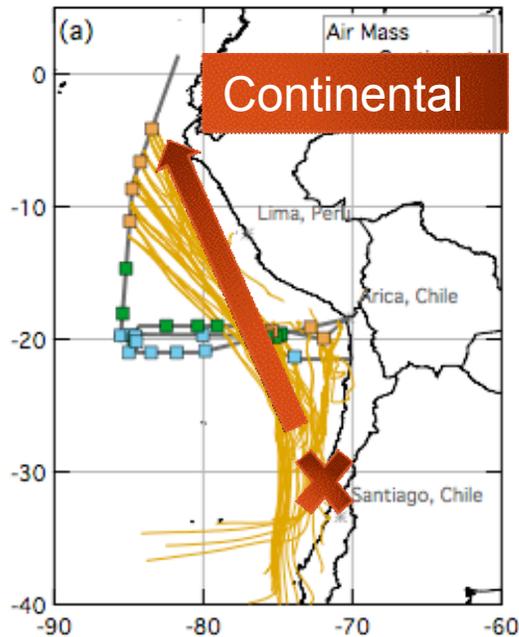
³Pacific Marine Environmental Laboratory, NOAA

Hawkins et al., 2009, *in prep.*

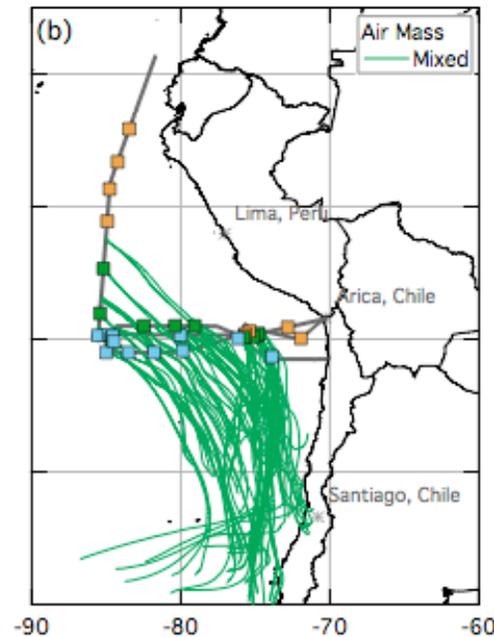
RONALD H. BROWN

AIR MASS SECTORS BY RADON

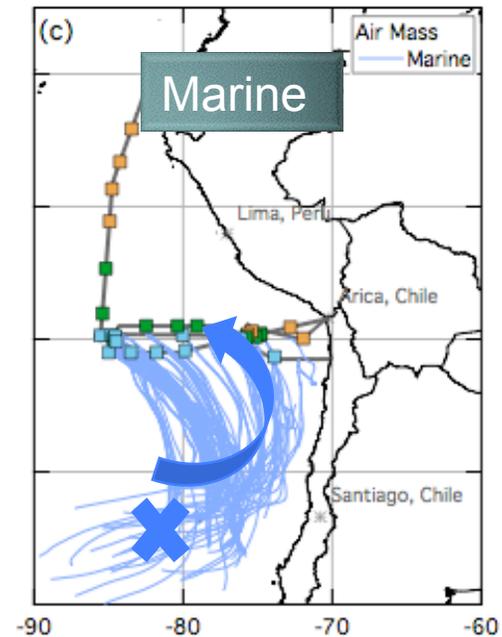
HYSPLIT 3-day back trajectories (50 masl, 100 masl, and 500 masl)



High radon,
recent (< 3 days)
continental contact



Intermediate radon



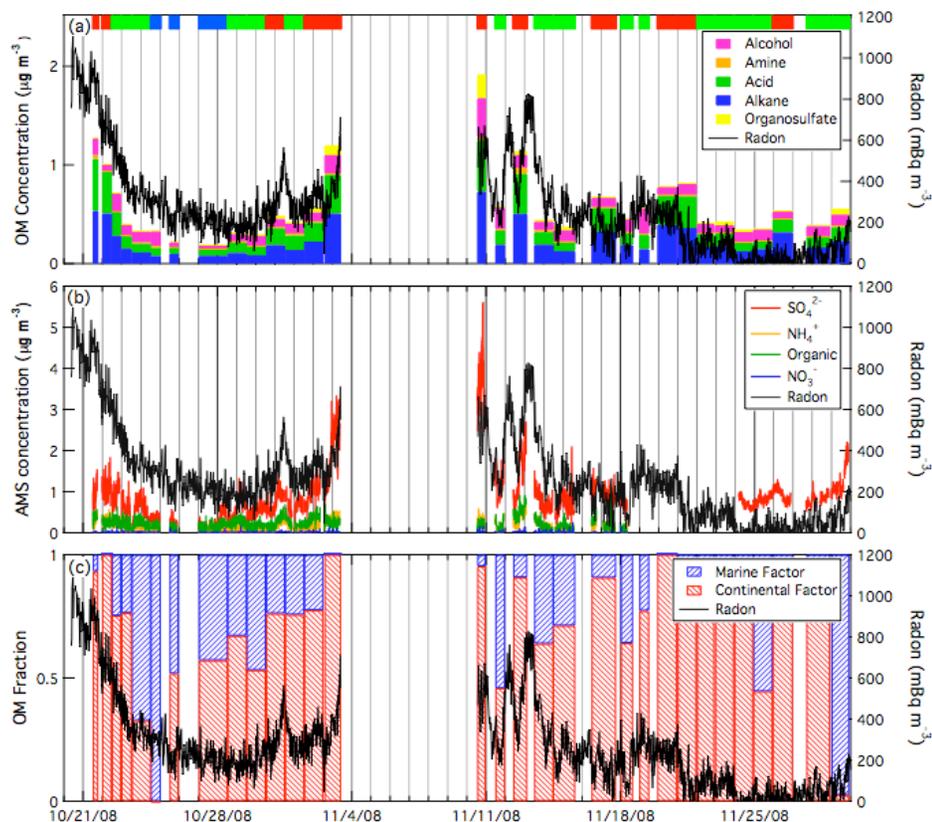
Low radon,
> 3 days
continental
contacts

REPORTED SIGNATURES OF FINE PARTICLE SOURCES IN SANTIAGO, CHILE

Particles < 2 μm were analyzed for black carbon and elemental concentrations

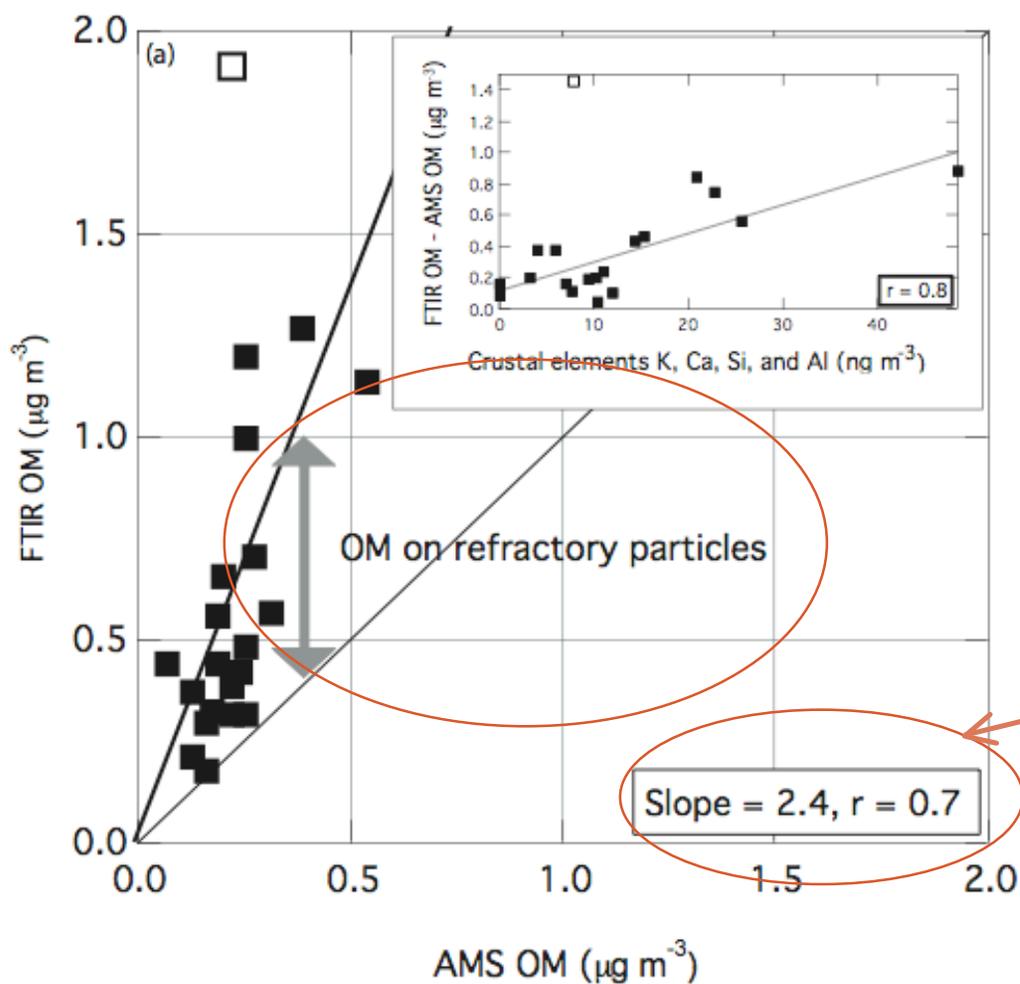
- Copper smelting, coal combustion, residual oil combustion
 - sulfur (as SO_2 oxidized to SO_4^{2-}), vanadium, and nickel
- Transportation (buses, cars, etc.)
 - potassium, bromine, and tin
- Resuspended soil dust (“direct traffic emissions are generally mixed with soil dust”)
 - calcium and iron

SUBMICRON PARTICLE COMPOSITION FROM FTIR SPECTROSCOPY AND AMS



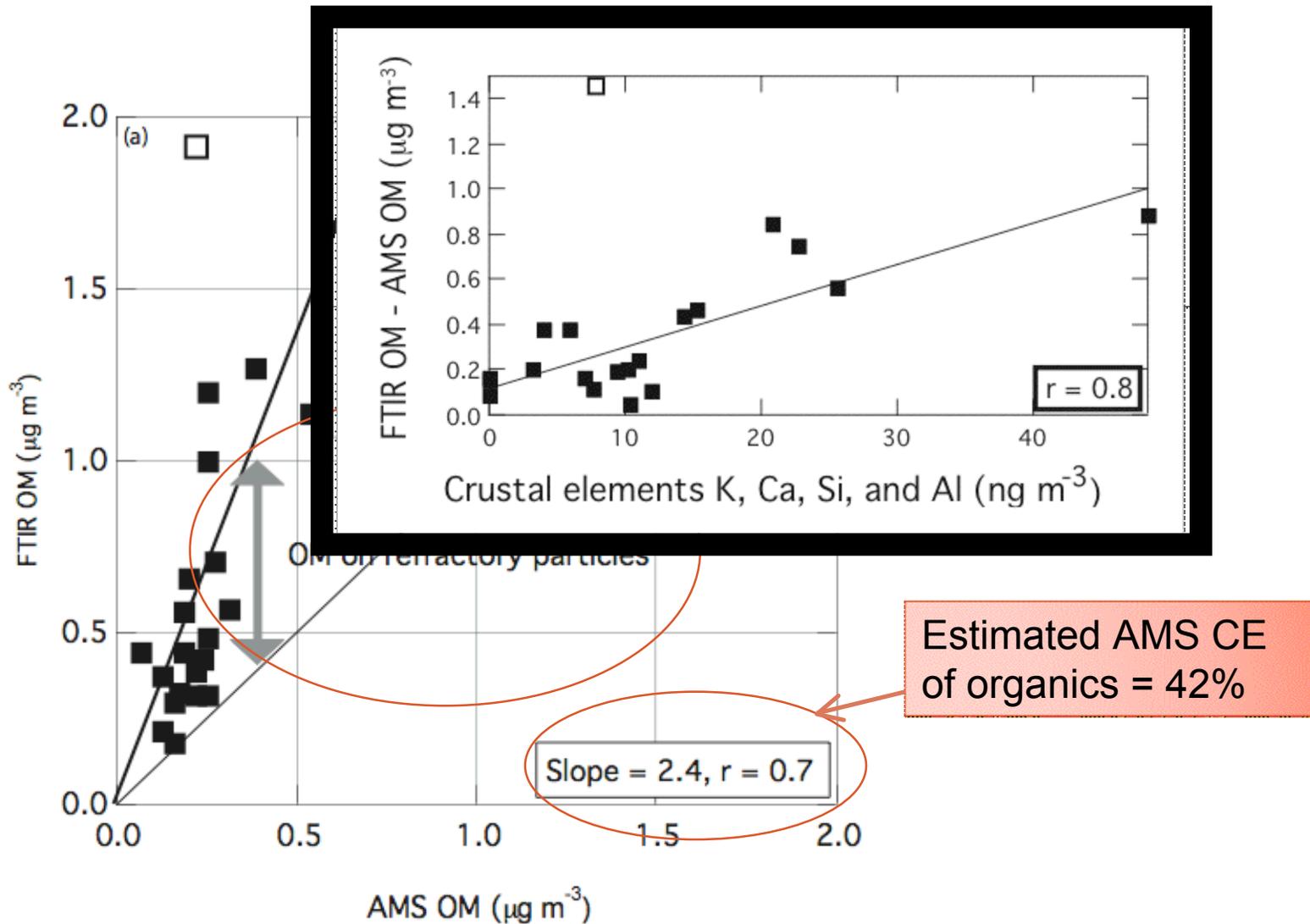
- PM_1 generally follows radon
- AMS SO_4^{2-} and FTIR OM show similar time trends
- AMS OM does not

REDUCED COLLECTION EFFICIENCY (CE) OF ORGANICS ON REFRACTORY PARTICLES (DUST)

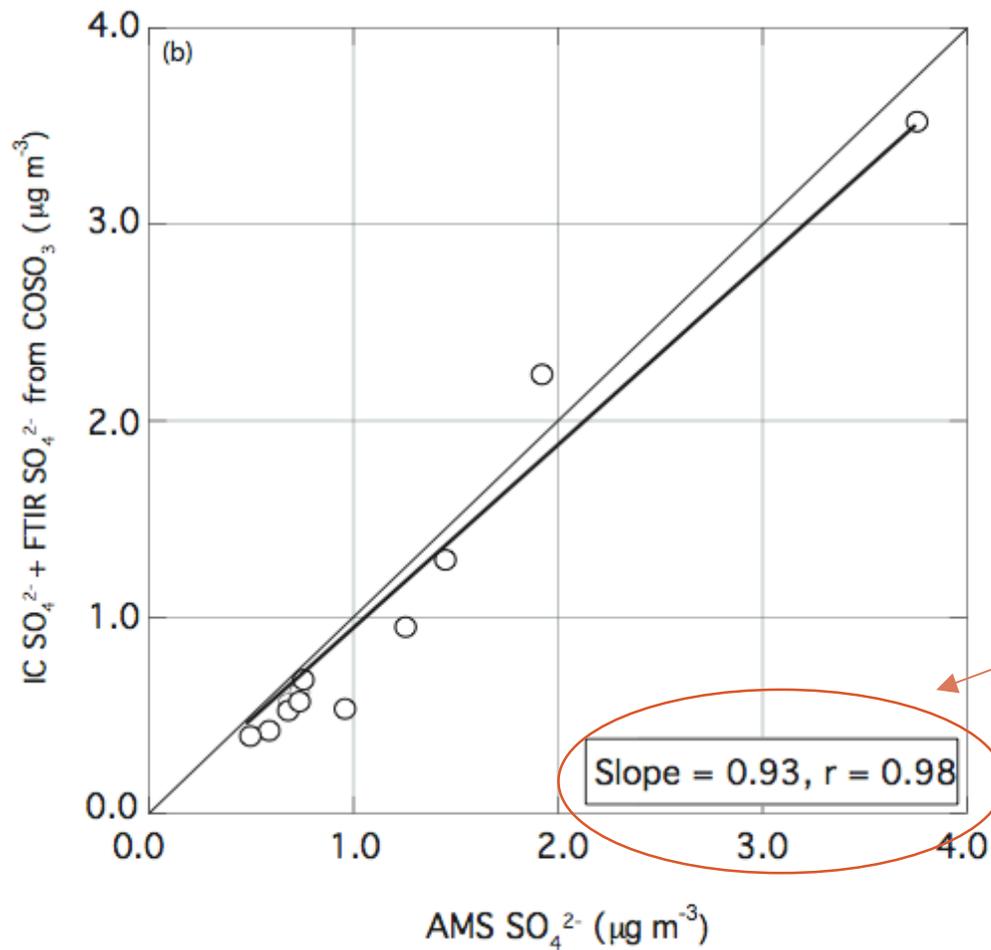


Estimated AMS CE
of organics = 42%

REDUCED COLLECTION EFFICIENCY (CE) OF ORGANICS ON REFRACTORY PARTICLES (DUST)



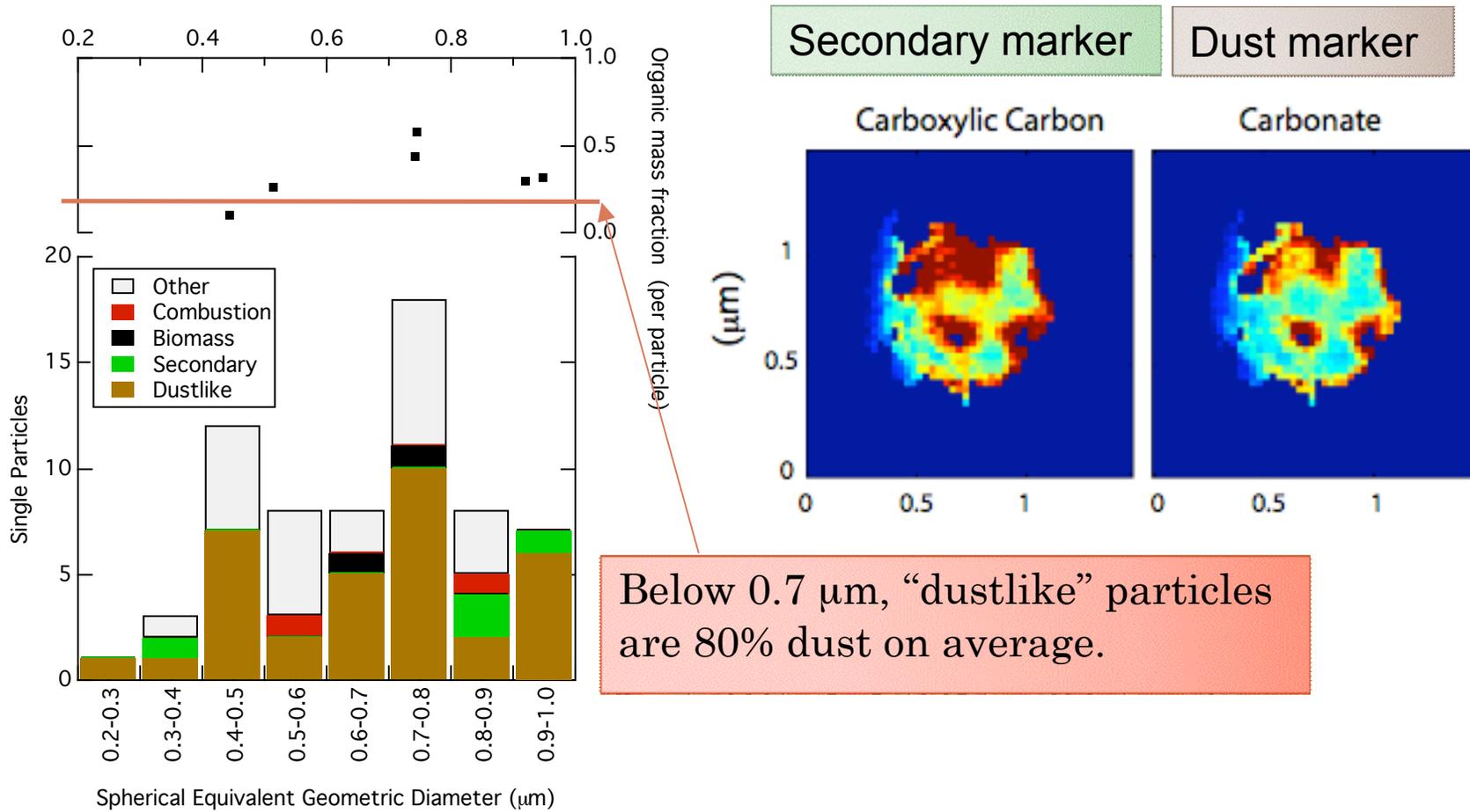
AMS CE OF SO_4^{2-} FROM IC SO_4^{2-}



○ Sulfate varied from acidic (no ammonium) to bisulfate.

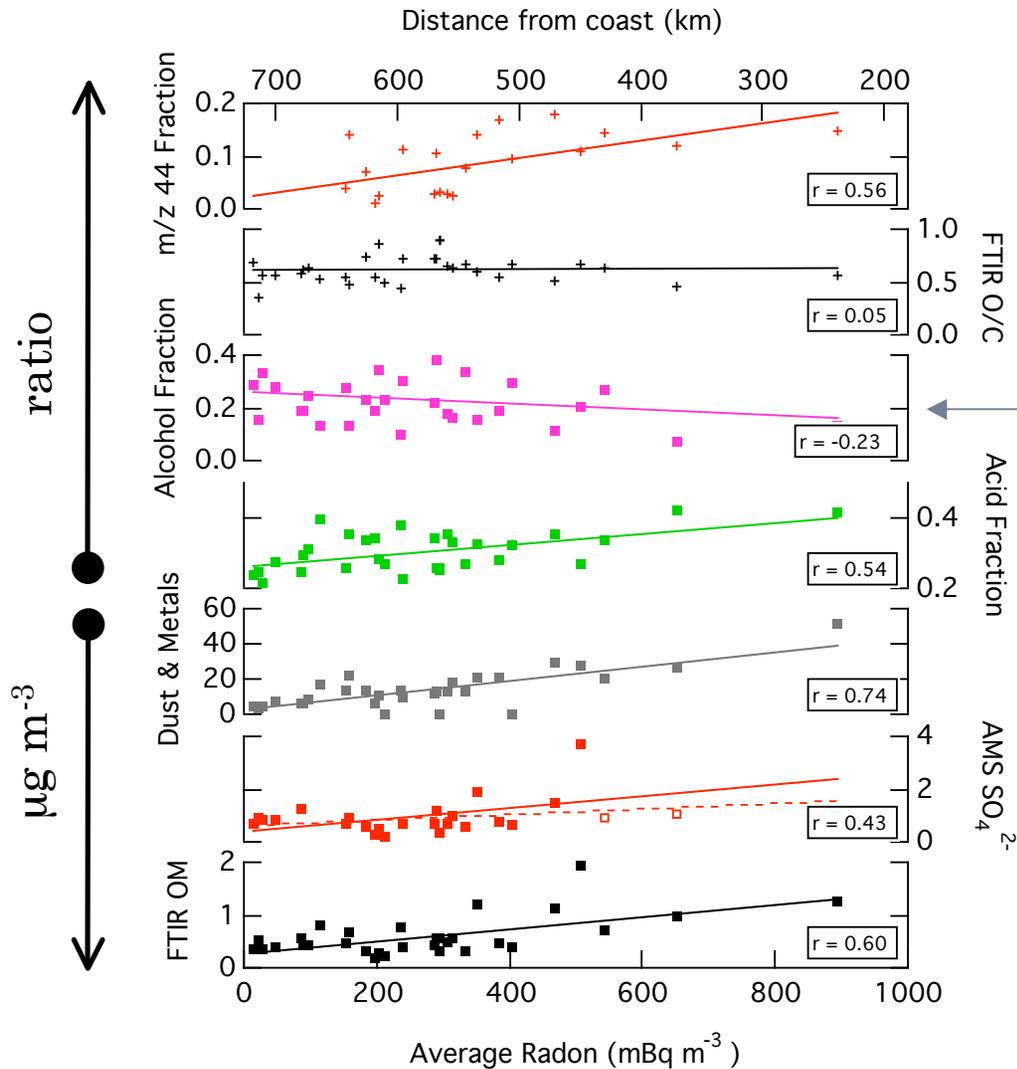
Estimated AMS CE of sulfate = 100%

SINGLE PARTICLE MEASUREMENTS FROM STXM-NEXAFS (X-RAY MICROSCOPY)



Takahama et al., 2007;2009

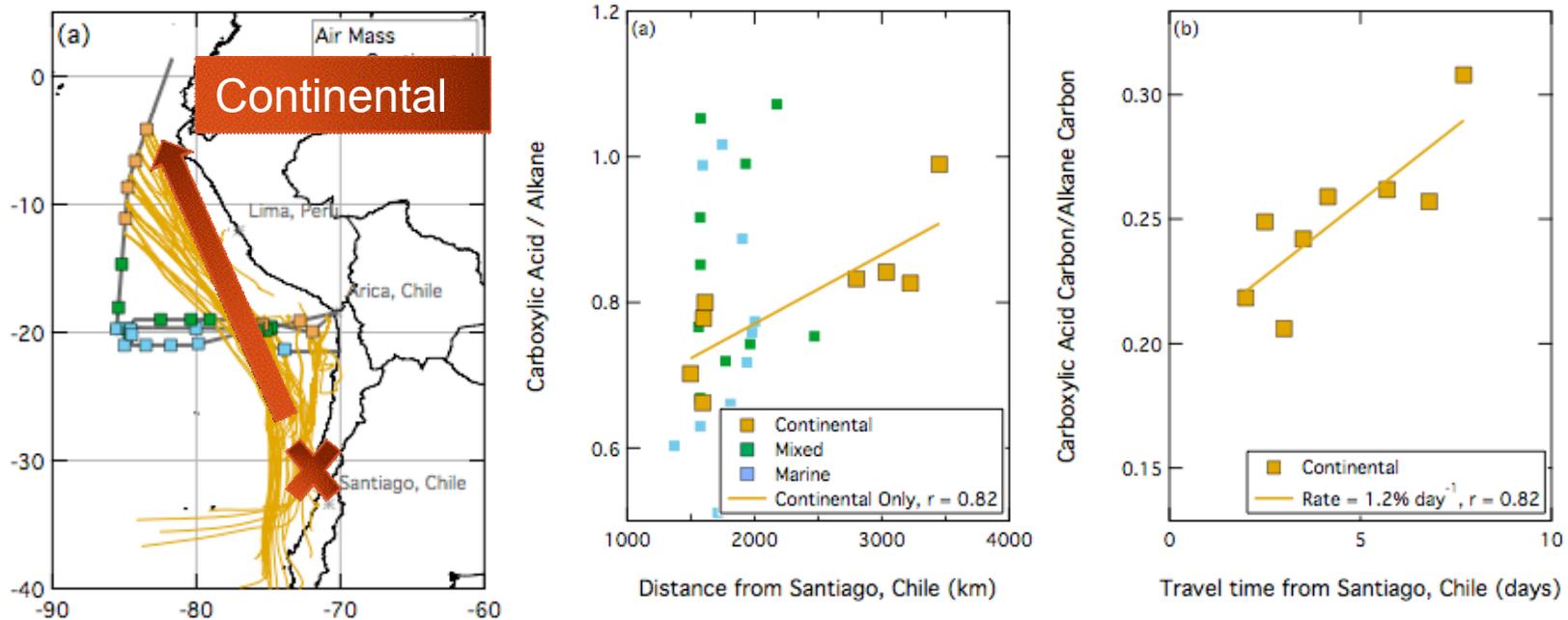
CONTINENTAL SOURCE OF PM₁ TO THE VOCALS STUDY REGION



No (v. weak inverse) correlation with radon implies marine source

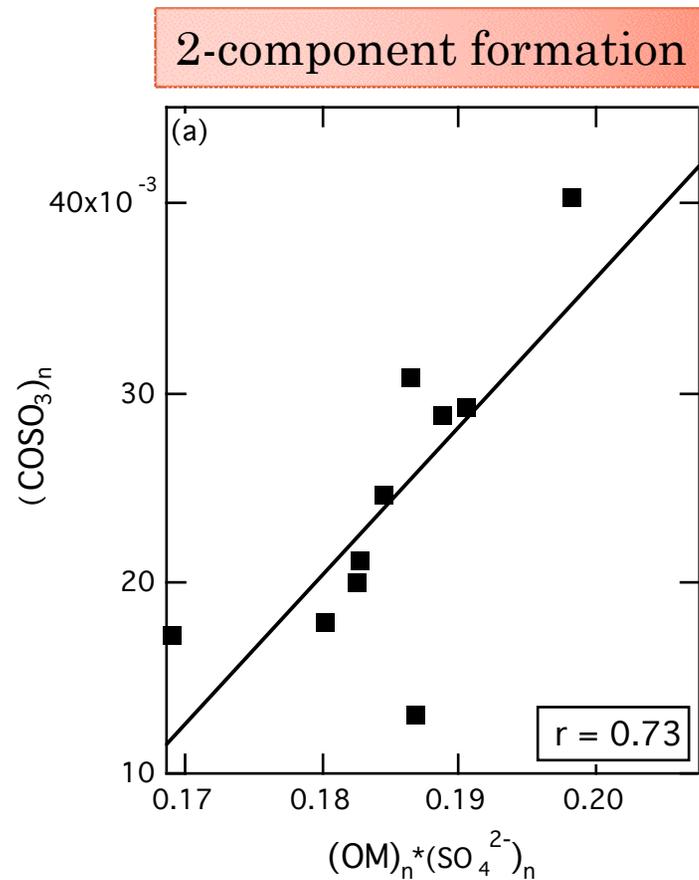
Positive correlations with radon imply continental source

EVIDENCE FOR AGING OF CONTINENTAL ORGANIC AEROSOL

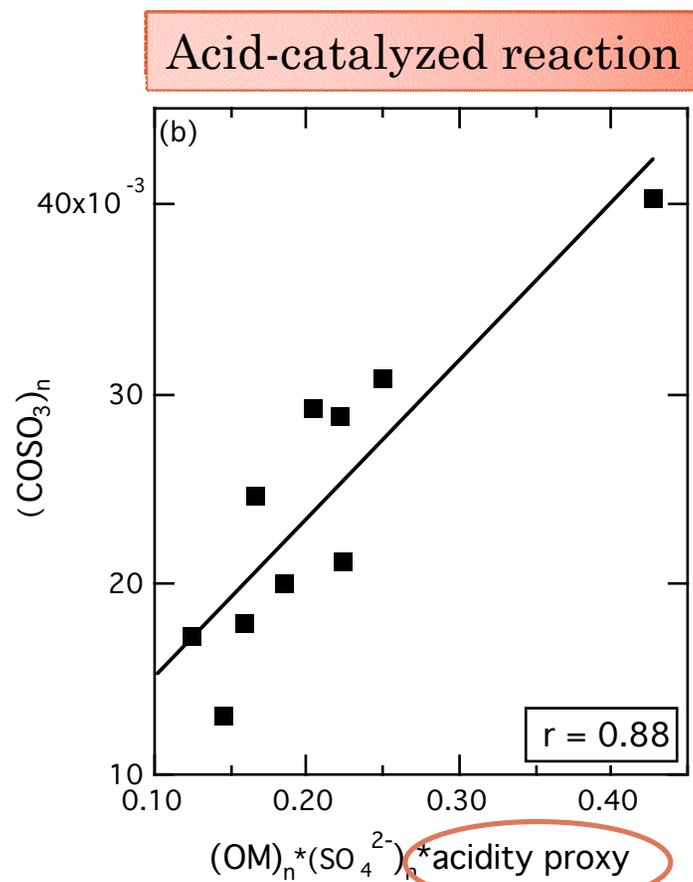


Low rate of oxidation is consistent with low O_3 (25 ± 4 ppb average, compare to 75 ppb EPA 8-hour standard) measured on board the RHB (away from Santiago).

ORGANOSULFATE FORMATION: TRENDS WITH $\text{SO}_4^{2-}/\text{NH}_4^+$ AND RH



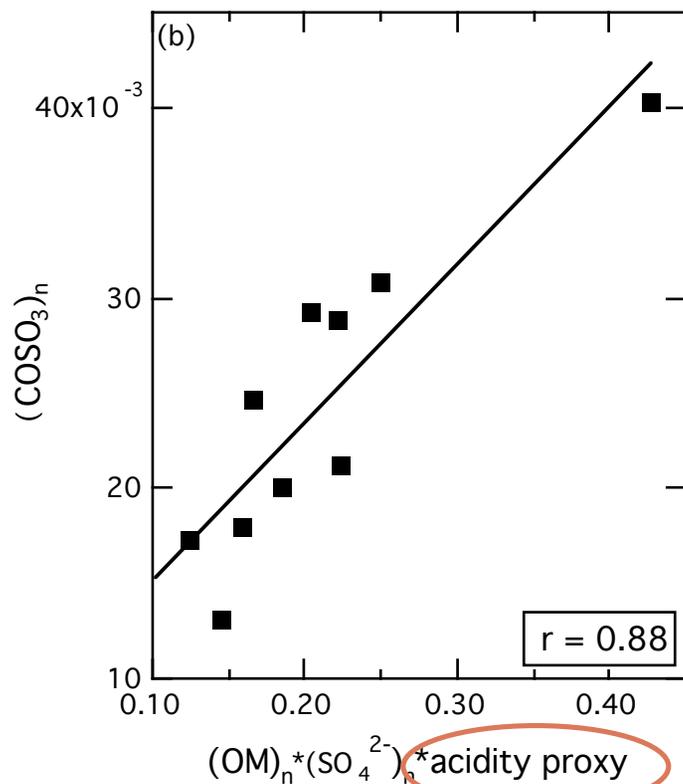
ORGANOSULFATE FORMATION: TRENDS WITH $\text{SO}_4^{2-}/\text{NH}_4^+$ AND RH



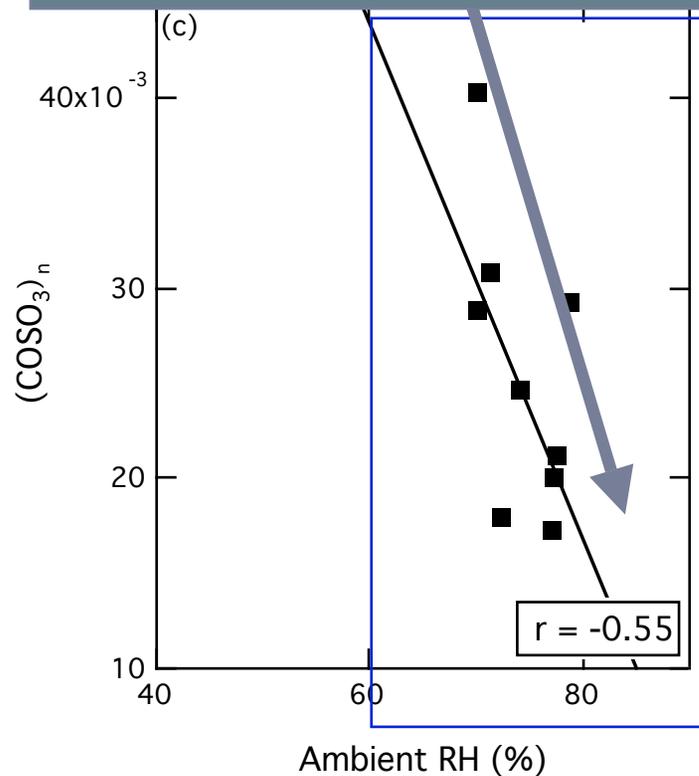
Defined as AMS $\text{SO}_4^{2-}/\text{NH}_4^+$

ORGANOSULFATE FORMATION: TRENDS WITH $\text{SO}_4^{2-}/\text{NH}_4^+$ AND RH

Acid-catalyzed reaction



Formed in cloud processing, but removed during scavenging, rainout

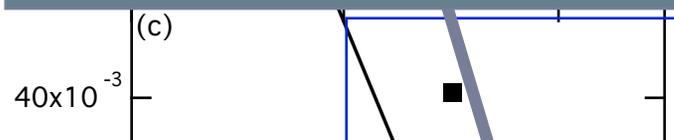
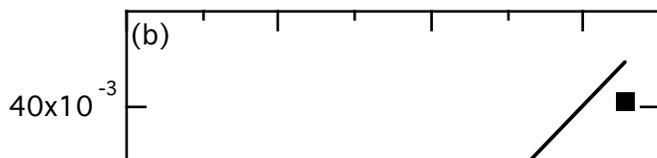


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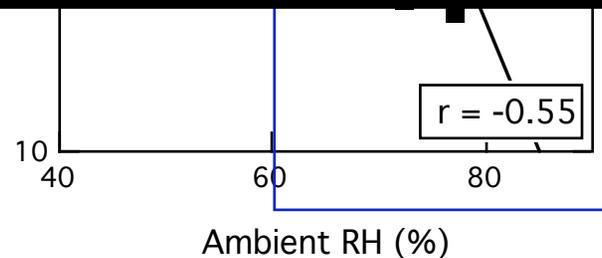
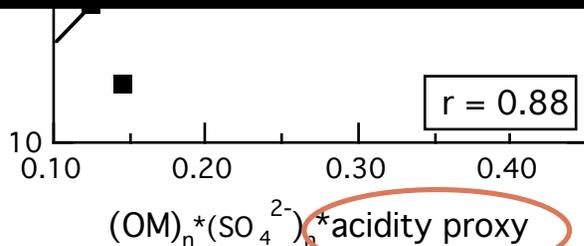
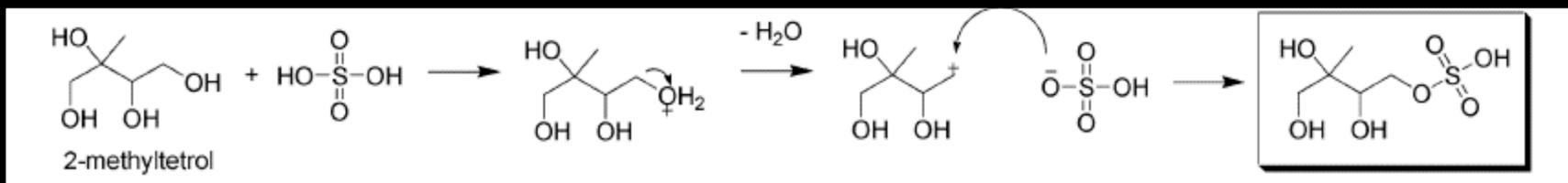
ORGANOSULFATE FORMATION: TRENDS WITH $\text{SO}_4^{2-}/\text{NH}_4^+$ AND RH

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Surratt et al., 2007b



Defined as AMS $\text{SO}_4^{2-}/\text{NH}_4^+$

Surratt et al., 2007a,b; Altieri et al., 2009

CONCLUSIONS FROM RHB AEROSOL CHEMISTRY

- Continental outflow of organic, sulfate, and dust components is main PM_{10} source.
- Santiago (and similar cities) are large contributors.
- Aging in continental air masses was slow (low ozone).
- Organosulfate increases with organics, sulfate, and acidity and decreases with RH.

