ACTAS

II SIMPOSIO SUDAMERICANO DE GEOLOGIA ISOTOPICA

II SOUTH AMERICAN SYMPOSIUM ON ISOTOPE GEOLOGY

II SSAGI

Argentina 1999

SUBSECRETARÍA DE MINERÍA DE LA NACIÓN

ISSN 0328-2325

CORDOBA 1999

INSTITUTO DE GEOLOGÍA Y RECURSOS MINERALES

SEGEMAR
SERVICIO GEOLÓGICO MINERO ARGENTINO

ANALES XXXIV

ATMOSPHERIC PARTICLES FROM SANTIAGO DE CHILE: $^{87}Sr/^{86}Sr$ AND $^{143}Nd/^{144}Nd$ ISOTOPIC RATIOS AND THEIR RELATIONSHIP WITH THE CRUSTAL RESERVOIR.

Mercedes Díaz[1], Kawashita Koji[2], Kei Sato[2] and. Carlos Roeschmann[1]

1 Servicio Nacional de Geología y Minería. Til-Til 1993. Ñuñoa. Santiago de Chile. mdiazver@yahoo.com., croeschm@sernageomin.cl.

2 Instituto de Geociências, Universidade de São Paulo. Rua do Lago 562. Cidade Universitaria. CEP 05508-900 São Paulo, Brazil. kaka@USP.br , keisato@USP.br

Keyboards index: environmental geology, urban air pollution, Sr isotopic ratios, Nd isotopic ratios.

INTRODUCTION

Santiago de Chile has a population over 4 million and is located in a poorly ventilated valley at 33°30'latitude south at an altitude of about 550m. Local climate is semi-arid with a mean annual rainfall below 350mm. The problem of air pollution in Santiago is compounded by the phenomena of ground-level and altitude thermal inversion (Romero, 1986). The ground level thermal inversion is visually evident on many days from late February through late November.

Atmospheric particles constitute one of the main factors of urban air pollution in the city. Their major natural source is the Earth's crust (Díaz *et al.*, 1998). The continental aerosol contain mainly materials from the nearby surface sources, somewhat modified by the coagulation of particles of different origin and by condensation products resulting from gas-phase reactions. The chemical composition of the urban continental aerosol reflect the relative global contributions of elements from the natural reservoirs and antropogenic sources. Isotopic composition must provide informations of the contribution from the diferent sources.

Once the crustal material has been brocken or eroded to grains sizes less than 1mm can be moved by wind forces. Most of these particles return quickly to the ground by gravitational settling. Only particles with radii smaller than 100 µm can remain airborne for a longer period of time, provided that they escape the surface friction layer due to turbulent air motion. With increasing wind speed, mobile particles will first creep or roll before they are temporarily lifted off the ground. Fine particles encrusted onto the coarser grains are loosened, break off, and a fraction of them gets thrown into the air. Shales have been considered as a reference material in atmospheric particles studies, with the argument that clays and silts migth better approximate soil substances susceptible to aerosol formation. The relative abundances of the major elements in the aerosol must not differ greatly from those in bulk soil and crustal rock average. (Rahn, 1975)

Because the major composite sampling process of the crust occurs during the weathering and erosion of the exposed rocks and late, during transportation and deposition of clastic sediments was considered that the geological processes of sedimentation produce an average sample of the exposed crust in the studied area. Sediments of the Mapocho River, Maipo River and Zanjon de la Aguada River have been sampling to compare the Sr and Nd isotopic ratios with those of atmospheric inorganic particles.

SAMPLING

The samples belong to two groups: particulate air material and river sediments.

URBAN AIR SAMPLES

The samples were collected in a outdoor air quality monitoring stations localized in two places of the Santiago City (M and D stations. (See Fig 1) during October 1996, February and May 1997. They were collected using a Sierra Instrument Model 244 Dichotomous Sampler (Virtual Impactor); suspended particles were sampled and size fractionated into two size fractions - 2.5 to 15 µm and less than 2.5 µm. The two particle fractions were collected uniformly on two 37 mm teflon membrane filters. The particulate material mass was determined weighting each filter before and after their exposure to the air (Fig.2). These filter are changed daily every 24 hours or as soon as the filters become saturate. Three monthly composites were prepared of each monitoring station with the fine and coarse filters belonging to October, February and May.

RIVER SEDIMENTS

The Río Mapocho (Mch), Río Maipo (Mp) and Zanjon de la Aguada River (Z) sediments were sampled using the techniques described by Antinao (1998) (see fig.1). The dried samples were screened and the fraction 400 ASTM (37μm) was selected for the present study.

EXPERIMENTAL PROCEDURES

Sr and Nd Isotopic natural ratios and Sr and Nd isotopic dilution from the environmental and sediments samples were determined.

PARTICULATE AIR MATERIAL

The fine and coarse teflon filters membrane were separated from the plastic frame and digested with a warm $HF-HNO_3$ solution during seven to ten days, dried down under I.R. lamp and finally redissolved in 6.0N HCl. The Sr and REE dissolved in a 2.5N HCl solution, were separated from the others constituents by a cation exchange procedure using a quartz column with AG 50W X8 (200-400 mesh) resin. The fraction enriched in ligth REE was loaded onto a second column prepared mixing Di (2ethylhexyl) ortophosphoric acid and teflon powder. More detailed procedure is described by Sato *et. al.* (1995).

SEDIMENTS

The fractions smaller than 37μm were attack with $HF-HNO_3$, evaporate to dryness and finally redissolved in 6.0N HCl. Sr and REE were separate from each other with the same techniques used for particulate air material.

TI-MASS SPECTROMETRY

The Sr and Nd isotopic compositions were measure using either a Finigam Mat 262 or a VG 354 mass spectrometer, both multicollector instruments. The Sr and Nd ratios measure in static mode analysis were normalized assuming $^{86}Sr/^{87}Sr$ = 0,1194 and $^{143}Nd/^{144}Nd$ = 0,7219.

RESULTS AND CONCLUSION

The daily mass average graphical representation shows the variations of coarse and fine atmospheric particles per volume unit because of antropogenic activities, air circulation at ground-level and altitude thermal inversion (Fig. 2). The fine fraction is more affected not only at the ground-level and to altitude thermal inversion but, also by coagulation and condensation processes. The air-borne clay fraction could take part with their actives spaces started by wet environmemt. Despite of heterogeneities in fine to coarse fractions and also to Sr/Nd ratios (Fig. 3), the isotope composition in air particulate materials are more uniform than exhibited by rivers sediments. The average ratios of 0.70590 for $^{86}Sr/^{87}Sr$ and 0.51255 for $^{143}Nd/^{144}Nd$ could be assumed provisorily in calculations involving blanks of these elements.

The Sr and Nd contents, and also their isotope ratios in the three rivers sediments are presented in Fig. 4. The Maipo River sediment exhibit very uniform isotope ratios for Sr and Nd. The average values of 0.70525 and 0.51263, respectively, when plotted in a Nd versus Sr ratios diagram fall close to Mantle Array line proposed, for example by Faure (1986). In contrast, the other sediments from Mapocho and Zanjon de la Aguada rivers present two groups of ratios: a lower of 0.7038 and another higher than 0.7052. However both groups show $^{143}Nd/^{144}Nd$ ratios *ca.* 0.56127 fitting also in the Mantle Array field. These last two groups, could be probably explained in terms of nature of the sediments. It is well known that the Sr released by chemical weathering of polymineralic rocks does not have exactly the same isotopic composition as in the original rock.. Sr is lost more readily from rocks exposed to weathering than Rb and $^{87}Sr/^{86}Sr$ ratio is generally lower than the $^{87}Sr/^{86}Sr$ ratio of the unweathered rocks.

In conclusion, the air particulate materials, modern sediments and, probably the suspended particulate materials and dissolved Sr and Nd elements, of Santiago area show Sr and Nd isotope composition which is characteristic of Mantle Array defined by MORB and series of oceanic island basalts (OIB).

REFERENCES

Antinao, J. L., 1998. Caracterización química de la contaminación ambiental en la Cuenca de Santiago mediante analisis de metales pesados en la fracción fina de sedimentos fluviales. Tesis de Magister. Departamento de Geología. Facultad de Ciencias Físicas y Matemáticas. Universidad de Chile.

Diaz, M., Kawashita,K., Fonseca, E., Roeschmann, C., Silva,Y., Olaeta, I., Olivares, G., Mannheim, R, 1997. Evidencias de material de origen geológico en el material particulado del aire de Santiago. Congreso Geológico Chileno.Antofagasta. 13-17 Octubre.

Faure, G., 1986. Principles of Isotope Geology. John Wesley & Son, 589p.

Rahn, K. A., 1975. Chemical Composition of atmospheric aerosol. A compilation II. Extern, 4, 639-667.

Romero, H., 1986. The topoclimatology of Santiago Basin. Frib. Geogr. Hefte. 26. 120-130.

Schütz, L., Rahn, K. A., 1982. Trace element concentration in erodible soils. Atmos. Environ. 16, 171-176.

Sato, K., Tassinari, C.C. G., Kawashita, K., Petronilho, L., 1995. O Método Geocronológico Sm-Nd no IG/USP e suas Aplicações. Annais Academia Brasileira Ciencias. 67(3): 313-336.

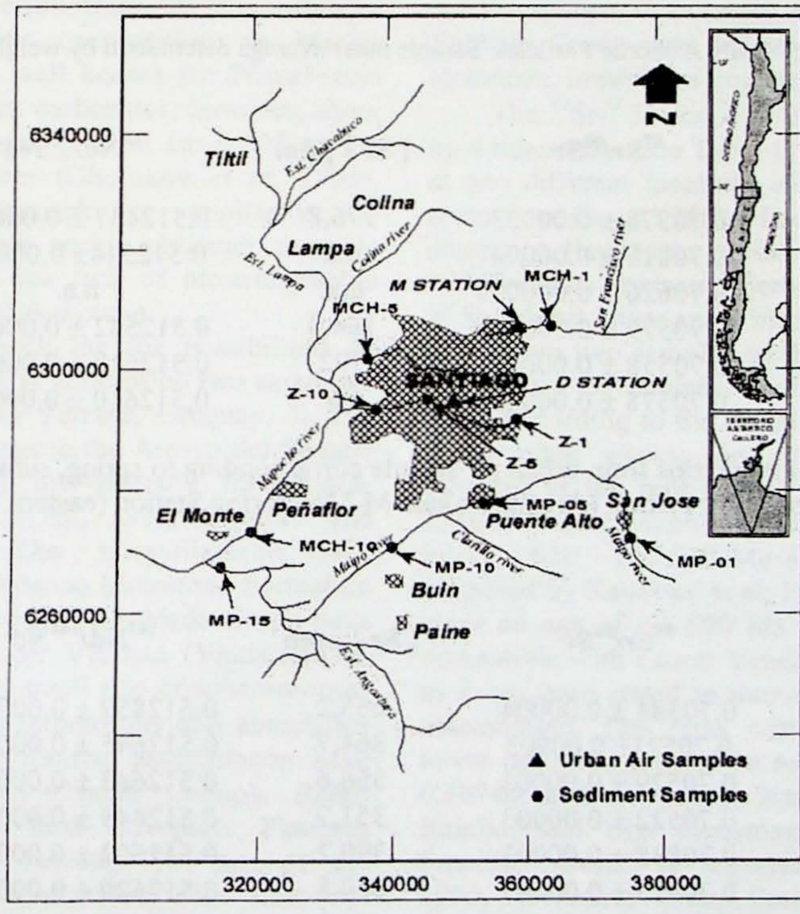

Figura 1: Samples and monitoring stations locality map.

Sample	Fraction	Mass/24 hours
1096D	Coarse	0.00098 ± 0.00026
1096D	fine	0.00056 ± 0.00022
0297D	Coarse	0.00130 ± 0.00028
0297D	fine	0.00057 ± 0.00014
0597D	Coarse	0.00146 ± 0.00058
0597D	fine	0.00147 ± 0.00075
1096M	Coarse	0.00101 ± 0.00028
1096M	fine	0.00050 ± 0.00017
0297M	Coarse	0.00110 ± 0.00028
0297M	fine	0.00050 ± 0.00012
0597M	Coarse	0.00113 ± 0.00050
0597M	fine	0.00113 ± 0.00062

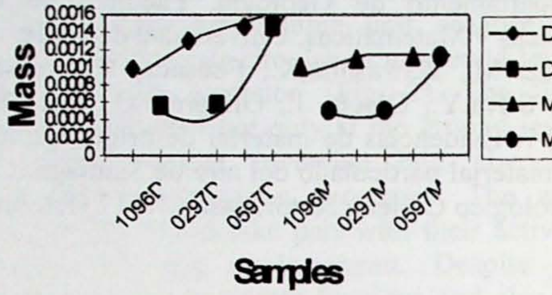

Figura 2: Daily Airborne Particles Sample mass average determined by weighting.

Sample	$^{87}Sr/^{86}Sr$	[Sr] ppm	$^{143}Nd/^{144}Nd$	[Nd] ppm
1096D	0.70578 ± 0.00003	176,8	0.512437 ± 0,000010	n.a.
0297D	0.70619 ± 0.00004	n.a	0.512544± 0.000070	28,00
0597D	0.70626 ± 0.00003	n.a.	n.a.	n.a.
1096M	0.70579 ± 0.00016	164,4	0.512542 ± 0,000010	6,27
0297M	0.70558 ± 0.00003	192	0.512618 ± 0,000010	26,70
0597M	0.70578 ± 0.00003	n.a.	0.512610 ± 0,000010	n.a.

Figure 3: Isotopic ratios from urban air sample corresponding to spring, summer and autumn. D-Monitoring Station (downtown)and M-Monitoring Station (eastern Santiago).

Sample	$^{87}Sr/^{86}Sr$	[Sr] ppm	$^{143}Nd/^{144}Nd$	[Nd] ppm
Mch-01	0.70384 ± 0.00004	265,2	0.512859 ± 0,000021	17,27
Mch-05	0.70521± 0.00003	364,7	0.512645 ± 0,000022	27,80
Mch10	0.70529 ± 0.00003	356,6	0.512663 ± 0,000020	21,96
Mp-01	0.70522 ± 0.00003	351,7	0.512649 ± 0,000020	25,85
Mp-05	0.70538 ± 0.00003	390,2	0.512602 ± 0,000020	25,79
Mp-10	0.70523 ± 0.00003	660,8	0.512620 ± 0,000020	29,11
Mp-15	0.70518 ± 0.00003	446,0	0.512645 ± 0,000025	28,78
Z-01	0.70339 ± 0.00004	334,4	0.512899 ± 0,000020	25,61
Z-05	0.70644 ± 0.00084	n.a.	0.512574 ± 0,000020	20.63
Z-10	0.70647 ± 0.00017	374,5	0.512644 ± 0,000020	23,50

Figure 4: Isotopic Ratios $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ from rivers sediments. Santiago de Chile.