

## Water Rock Interaction [WRI 14]

# Formation of a low-crystalline Zn-silicate in a stream in SW Sardinia, Italy

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### Abstract

In southwestern Sardinia, Italy, the Rio Naracauli drains a catchment that includes several abandoned mines. The drainage from the mines and associated waste rocks has led to extreme concentrations of dissolved Zn, but because of the near-neutral pH, concentrations of other metals remain low. In the reach from approximately 2300 to 3000 m downstream from the headwaters area, an amorphous Zn-silicate precipitates from the water. In this reach, concentrations of both Zn and silica remain nearly constant, but the loads (measured in mass/time) of both increase, suggesting that new Zn and silica are supplied to the stream, likely from emerging groundwater. Zinc isotope signatures of the solid are heavier than the dissolved Zn by about 0.5 permil in <sup>66/64</sup>Zn, suggesting that an extracellular biologically mediated adsorption process may be involved in the formation of the Zn-silicate.

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## 1. Introduction

The influence of mining on the environment is well known [1, 2]. In general, mining increases dissolved metal loads in streams by bringing reduced sulfide minerals to the surface where they are exposed to the oxygenated weathering environment and by crushing rock, which enhances mineral surface areas and thus also enhances mineral dissolution/oxidation rates. In many cases, mining-impacted streams have low pH and high concentrations of metals and sulfate, most all of which are derived from the dissolution of sulfide-bearing minerals such as pyrite, sphalerite, etc. In cases where accessory

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minerals include carbonates such as calcite or rhodochrosite, pH may remain near neutral.

The Rio Naracauli drains an area with several abandoned mines in southwestern Sardinia, Italy [3]. The mines produced Zn and Pb, and quartz and carbonates are associated with the ore. The flow in Rio Naracauli is a few tens of liters per second, but the extreme Zn concentrations (up to 120 mg/L) result in Zn loads on the order of  $10^4$  kg/yr delivered to the Mediterranean Sea. On the other hand, because of the near-neutral pH, concentrations of Fe and Mn are generally  $<50$   $\mu\text{g/L}$  and Cu is generally  $<10$   $\mu\text{g/L}$ .

In the upstream reaches of the Rio Naracauli, hydrozincite  $[\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]$  forms in a biological adsorption - mineralization process [3,4]. The formation of hydrozincite in the stream ceases when the stream is diluted by a tributary about 600m downstream from the headwaters area. Further downstream, there is a large waste dump, and below that, from 2300-3000 m below the headwater spring, a Zn-silicate solid is forming in the streambed. This solid has a stoichiometry similar to willemite ( $\text{Zn}_2\text{SiO}_4$ ), but lacks long-range crystallographic order [9,10].

Zinc isotopes have been found to be useful to indicate both sources and processes related to Zn transport [5, 6]. Isotopic shifts of up to a permil in  $^{66/64}\text{Zn}$  have been seen in cases where Zn adsorbs onto organic material or inorganic substrates. In a previous study [7], hydrozincite in Rio Naracauli was found to be approximately 0.35 ‰ heavier in  $^{66/64}\text{Zn}$  than dissolved Zn in the water from which it formed. This isotopic shift was attributed to Zn adsorption and nucleation on the surface of a cyanobacterium, *Scytonema Sp.*, which plays an active role in hydrozincite nucleation and crystal growth.

The goals of this study were to characterize the Zn-isotopic composition of the water and Zn-silicate, and to characterize metal concentrations in water throughout the reach in which the Zn-silicate is forming.

### 1.1. Methods

Water and solid samples were collected from Rio Naracauli in October 2009 and June 2011. At each site, pH, specific conductance, and T ( $^{\circ}\text{C}$ ) were measured at the time of sampling. Water samples were 0.4  $\mu\text{m}$  filtered and collected as described previously [7]. Solids were collected by agitating precipitate-covered pebbles in a bottle of stream water and decanting the streamwater. Water samples were analysed by ICP-AES (major cations), ICP-MS (trace elements), IC (major anions), and Gran titration (alkalinity).

Zinc isotope analyses were conducted on a Nu Instruments high-resolution multicollector ICP-MS (MC-ICP-MS) in normal resolution mode (precision  $\pm 0.1$  ‰) following separations as described in [8]. Isotopes of Zn are generally expressed in conventional  $\delta$  notation, using the JMC 3-0749 Lyon standard:

$$\delta^{66}\text{Zn}, \text{‰} = \{(R_{\text{spl}}/R_{\text{std}}) - 1\} * 1000 \quad (1),$$

where R is the ratio of abundance of  $^{66}\text{Zn}/^{64}\text{Zn}$  and the subscripts spl and std refer to the sample and the JMC 3-0749 Lyon standard, respectively. See [7] for thorough details of the isotopic methods used.

In June 2011 a continuous-injection tracer experiment was conducted with synoptic sampling [11], allowing for the calculation of stream discharge as well as loadings of individual dissolved constituents. The tracer experiment involved spatially dense sampling, with seven stream samples and one tributary collected in the 700 meter reach of interest to this study. However, solid sampling was limited to the lowermost point of the study reach because fresh solid was most abundant and easily collected there.

## 2. Results

### 2.1. Chemistry of major and trace elements

The major-ion chemical character of the stream-waters is Ca-Mg-SO<sub>4</sub> with minor Cl, contributed by sulfide mineral weathering and proximity to the Mediterranean Sea and associated effects of aerosols in

sea spray. Metals such as Zn are derived from weathering of mine wastes in the Rio Naracauli drainage. Zinc is added to the stream throughout the study reach, as supported by the observation that although flow increases from 30 to 35 L/sec along the study reach, concentrations of Zn and other metals do not change dramatically (table 1). The increase in flow is likely due to discharge of metal-rich ground water that has passed through mine- and mill-waste material dispersed in the Rio Naracauli catchment.

Table 1 shows the results of selected chemical analyses and chemical modeling results for streamwater samples. Site numbers in the table are downstream distance from the headwater area of the Rio Naracauli. In the table, the ion activity product (IAP) of  $Zn_2SiO_4$  and saturation index (SI) values for chalcedony are shown as calculated using PHREEQC [12]. The Zn silicate in Rio Naracauli was described previously [9,10]. Recent X-ray absorption spectroscopy and HR-TEM investigations indicate that Zn-silicate has a low crystalline order and the local coordination environment of Zn matches that of willemite.

Table 1. Selected chemical analyses from the Rio Naracauli. All samples in this table were collected in June, 2011. Site numbers are distance downstream (m) from the headwater spring. Units are as follows: pH (dimensionless); Zn,  $SiO_2$  (mg/L);  $\delta^{66}Zn$  in permil (‰) relative to JMC 3-0749 Lyon, IAP of  $Zn_2SiO_4$  and SI for chalcedony (dimensionless).

Site number	pH	Zn conc	$SiO_2$ conc	$\delta^{66}Zn$	IAP $Zn_2SiO_4$	SI Chalcedony
2320	7.93	11.5	23	-1.02	19.8	-0.02
2410	7.89	12.2	23.4	-1.07	19.7	-0.02
2485	7.94	11.7	22.6	nm	19.8	-0.03
2565	7.86	11.7	22.4	nm	19.5	-0.04
2665	7.92	11.8	22.5	nm	19.7	-0.03
2785	7.88	11.0	21.4	-1.29	19.5	-0.05
2946	7.92	11.3	21.5	-1.37	19.7	-0.05

## 2.2. Zinc isotopes

Water and solid samples were collected for Zn isotope analyses, as described in the Methods section. Between 2009 and 2011, three pairs of water and solid samples were collected from the sample point at 2946 m. Results of the isotopic analyses are shown in Table 2. As seen in the table, the Zn in the solid is heavier by an average of 0.51 ‰ relative to the water.

Table 2. Zinc isotope analyses of water and solid samples collected at site 2946, expressed as  $\delta^{66}Zn$  in permil (‰) relative to the JMC 3-0749 Lyon standard. The value of  $\Delta_{solid-water}$  is the difference between the  $\delta^{66}Zn$  values for each of the water-solid pairs.

Date	$\delta^{66}Zn$ water	$\delta^{66}Zn$ solid	$\Delta_{solid-water}$
28 November 2009	-0.22	+0.25	0.47
14 June 2011	-1.35	-0.82	0.53
15 June 2011	-1.39	-0.86	0.53

## 3. Discussion and Conclusions

In the lower reaches of the Rio Naracauli, Zn concentrations are controlled by the formation of a low-crystalline Zn silicate. The solid has a stoichiometry similar to willemite ( $Zn_2SiO_4$ ), so the ion activity product (IAP) equals  $[Zn^{2+}]^2 * [H_4SiO_4^0] * [H^+]^{-4}$ . The IAP varies within a narrow range (Table 1),

suggesting that the Zn-silicate solid has approached steady state or possibly equilibrium. Values of SI for crystalline willemite range from 5.3 to 5.6, so the low-crystalline solid is much more soluble than crystalline willemite, as expected. Silica concentrations also may be controlled by chalcedony, consistent with  $SI_{\text{chalcedony}}$  values near zero (Table 1). A near-equilibrium process for Zn-silicate formation also is suggested by the relatively narrow range of  $\Delta_{\text{solid-water}}$  (Table 2). Consistent with earlier work [5,7], the fact that the solid incorporates the heavier isotope suggests either an extracellular biological-adsorption process, or an inorganic adsorption-dominated mechanism [13]. There is a significant temporal shift in  $\delta^{66}\text{Zn}$  in both the water and solid from 2009 to 2011. This seasonal shift may be due to climatic variations, which could change the hydrologic regime and thus change Zn sources.

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## References

- [1] Nordstrom DK, Alpers CN. Geochemistry of acid mine waters. In: Plumlee, GS, Logsdon, MJ, eds. *Environmental Geochemistry of Mineral Deposits, Reviews in Economic Geology 6A*, Chelsea: Economic Geology Publishing Co.; 1999.
- [2] Younger PL, Banwart SA, Hedin RS. *Mine Water: Hydrology, Pollution, Remediation* Dordrecht: Kluwer Academic Publishers; 2002.
- [3] Medas D, Cidu R, Lattanzi P, Podda F, Wanty RB, De Giudici G. Hydrozincite seasonal precipitation at Naracauli (Sardinia-Italy): Hydrochemical factors and morphological features of the biomineralization process. *Appl Geochem* 2012; **27**: 1814-1820.
- [4] Podda F, Zuddas P, Minacci A, Pepi M, Baldi F. Heavy metal coprecipitation with hydrozincite  $[\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]$  from mine waters caused by photosynthetic microorganisms. *Appl Environ Microbiol* 2000; **66**: 5092-5098.
- [5] Cloquet C, Carignan J, Lehmann MF, Vanhaecke F. Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review. *Anal Bioanal Chem* 2008; **390**: 451-463.
- [6] Borrok DM, Wanty RB, Ridley WI, Lamothe PJ, Kimball BA, Verplanck PL, Runkel RL. Application of iron and zinc isotopes to track the sources and mechanisms of metal loading in a mountain watershed. *Appl Geochem* 2009; **24**: 1270-1277.
- [7] Wanty RB, Podda F, DeGiudici GB, Cidu R, Lattanzi P. Zinc-isotope and transition-element dynamics accompanying hydrozincite biomineralization in the Rio Naracauli, Sardinia, Italy. *Chem Geol* (in press).
- [8] Borrok DM, Wanty RB, Ridley WI, Wolf RE, Lamothe PJ, Adams M. Separation of copper, iron, and zinc from complex aqueous solutions for isotopic measurement. *Chem Geol* 2007; **242**: 400-414.
- [9] Zuddas P, Podda F, Lay A. Flocculation of metal-rich colloids in a stream affected by mine drainage. In: Arehart, GB, Hulston, JR, editors. *9<sup>th</sup> International Symposium on Water-Rock Interaction*, Rotterdam: Balkema; 1998; 1009-1012.
- [10] Medas D, Cidu R, Lattanzi P, Podda F, De Giudici G. Natural biomineralization in the contaminated sediment-water system at the abandoned mine of Ingurtosu. In: Kothe, E, Varma, A, editors. *Bio-geo Interactions in Metal-Contaminated Soils*, Heidelberg: Springer; 2012; 113-130
- [11] Kimball BA, Runkel RL, Walton-Day K, Bencala KE. Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling- Cement Creek, Colorado, USA. *Appl Geochem* 2002; **17**: 1183-1207.
- [12] Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (V2)- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *US Geol Surv Water-Resource Inv Report 99-425*; 1999.
- [13] Balistrieri LS, Borrok DM, Wanty RB, Ridley, WI. Fractionation of Cu and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental mixing of acid rock drainage with ambient river water. *Geochim Cosmochim Acta* 2008; **72**: 311-328.