

# Chapter 1

## Introduction

Zinc (Zn) atoms, regardless of isotope, have thirty protons in the nucleus and therefore have a similar configuration of electrons orbiting the nucleus. The chemistry of Zn is determined mostly by the interactions of these protons and electrons with each other and with charged particles of other atoms. The difference between Zn isotopes lies in the number of neutrons in the nucleus. Slight differences in nuclear mass will have a small effect on the strength of the bonds that the atoms forms. Slight differences in the bonding strength of difference isotopes can lead to a preferential accumulation of heavy or light Zn isotopes in certain bonding environments. Zn isotope ratios therefore contain information about the chemical processes that have acted upon Zn atoms. The growth of phytoplankton in the oceans, chemical adsorption to sinking particles, the circulation of

seawater through hydrothermal vents, and other oceanographic processes involve changes in the chemical bonding of Zn. Zn isotopes therefore contain information about the chemical history of samples and may be valuable tracers of chemical oceanographic processes.

## **1.1 Historical overview**

### **1.1.1 The development of MC-ICP-MS**

The development of multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) has increased the ease and accuracy of isotope measurement for trace elements. Isotopic analysis by thermal ionization mass spectrometry (TIMS) is, in comparison, more time-consuming, less effective at ionizing transition metals such as Zn, and subject to errors based on the time-dependent fractionation of isotopes during evaporation from a filament. The accuracy of single-collector ICP-MS, in which different isotopes are measured in rapid succession, is limited by plasma instability, rapid variations in ionization efficiency on timescales less than the timescale of measurement. Multi-collector measurements correct for this by simultaneously collecting data on all masses of interest.

The development of MC-ICP-MS has led to an explosion in the study of “non-traditional” stable isotopes. Natural variations have been discovered in the stable isotopes of Cr, Fe, Cu, Zn, Mo, Cd, Hg, and many other elements (Anbar and Rouxel, In revision; Johnson et al., 2004).

### **1.1.2 Natural Zn isotopes in environmental and marine systems**

Figure 1 presents the natural Zn isotope measurements that had been reported at the time I proposed to undertake this thesis. Data on Zn isotopes in the ocean included measurements on manganese nodules and marine sediment trap material (Maréchal et al., 2000). Manganese nodules had generally higher Zn isotope ratios in polar regions than in low latitudes, an effect that was suggested to correlate with biological Zn uptake in the upper ocean (Fig. 2). Sediment trap data showed a remarkable seasonal signal in the Zn isotope composition of sinking particles (Chapter 6). Data showing large variations in the  $\delta^{66}\text{Zn}$  leached from bulk sedimentary carbonates over the last 175 ka suggested that Zn isotopes might have uses as a paleotracer for surface productivity (Pichat et al., 2003).

Several notable papers on Zn isotopes in marine and environmental systems have been published in the past few years. Zinc isotopes have been measured in ancient hydrothermal deposits (Mason et al., 2005; Wilkinson et al., 2005), air and lichen samples influenced by anthropogenic Zn (Cloquet et al., 2006; Dolgoplova et al., 2006), cultured phytoplankton (Gélabert et al., 2006), and seawater (Bermin et al., 2006).

### **1.2 Zinc stable isotope analysis**

Zinc has five stable isotopes:  $^{64}\text{Zn}$  (49.2%),  $^{66}\text{Zn}$  (27.8%),  $^{67}\text{Zn}$  (4.0%),  $^{68}\text{Zn}$  (18.4%), and  $^{70}\text{Zn}$  (0.6%) (Tanimizu et al., 2002). MC-ICP-MS can be used to measure the ratio of Zn isotopes in a sample. We measure  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ , and  $^{68}\text{Zn}$ , the three most dominant Zn isotopes. All isotopic measurements were made on an IsoProbe MC-ICP-MS. Typical

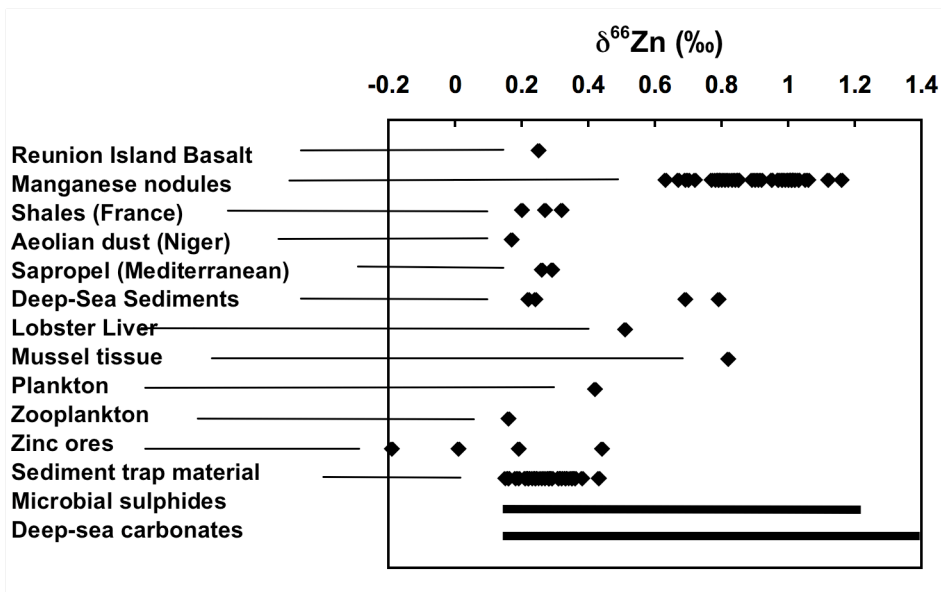


Figure 1.1. Published measurements of Zn isotopes in natural samples when this thesis began. Data is from (Maréchal et al., 2000), except for data on microbial sulfides (Archer and Vance, 2002), and deep-sea carbonates (Pichat et al., 2003).

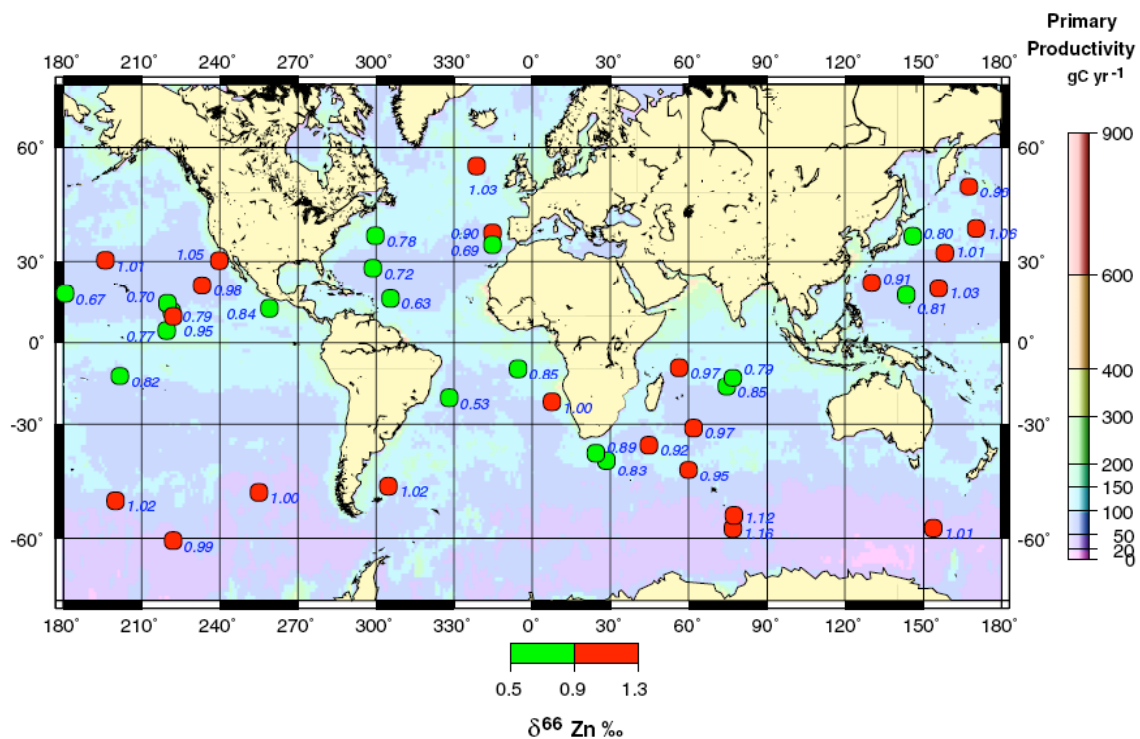


Figure 1.2. The Zn isotope composition of manganese nodules from around the world. From Maréchal et. al. (2000).

analytical conditions are shown in Table 1.

### 1.2.1 Conventions for reporting Zn isotope ratios

Zinc isotope data is typically reported in terms of the  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio of the sample in relation to the “Lyon – JMC standard” from the lab of Francis Albarède (Maréchal et al., 1999) according to the equation:

$$\delta^{66}\text{Zn} = \left( \frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{JMC standard}}} - 1 \right) \cdot 1000$$

Similarly, the ratio of  $^{68}\text{Zn}/^{64}\text{Zn}$  is reported as:

$$\delta^{68}\text{Zn} = \left( \frac{(^{68}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{68}\text{Zn}/^{64}\text{Zn})_{\text{JMC standard}}} - 1 \right) \cdot 1000$$

In this thesis, isotope effects (or any offset between the  $\delta^{66}\text{Zn}$  of two samples) are reported as:

$$\Delta^{66}\text{Zn} = \delta^{66}\text{Zn}_A - \delta^{66}\text{Zn}_B$$

where A and B are the two samples. This terminology is potentially confusing because  $\Delta$  terminology is also used to describe non-mass dependant mass fractionation of O, S, and Hg isotopes.  $\epsilon$  notation, often used to describe biological isotope effects in measurements

### **Typical IsoProbe operating conditions:**

Sample cone: Aluminum

Skimmer cone: Ni "X-cone"

Nebulizer: MicroMist glass nebulizer

Aspiration rate: 75  $\mu$ L/min, free draw

Desolvator: APEX Q

Desolvating membrane: none

Cool gas flow: 13-14 L/min

Intermediate gas flow: 0.9-1.0 L/min

Neb gas 1: 0.2-0.3 L/min

Neb gas 2: 0.7-0.9 L/min

Sample matrix: 2% (vol.) HNO<sub>3</sub>

Sample uptake time before measurement: 3 min

Data acquisition time: 3 min

Rinsing time between measurements: 6 min

<u>Collector</u>	<u>Mass</u>	<u>Predominant isotopes</u>
L1	60	<sup>60</sup> Ni
Ax	63	<sup>63</sup> Cu
H1	64	<sup>64</sup> Zn, <sup>64</sup> Ni
H3	65	<sup>65</sup> Cu
H4	66	<sup>66</sup> Zn
H5	67	<sup>67</sup> Zn
H7	68	<sup>68</sup> Zn

Table 1.1. Typical analytical conditions for Zn isotope analysis on the IsoProbe.

of  $\delta^{13}\text{C}$ , is inappropriate because  $\epsilon$  is also used in reporting Nd isotope measurements to signify that result is in parts-per-ten thousand. ‘ $\Delta\delta$ ’ notation, where:

$$\Delta\delta^{66}\text{Zn} = \delta^{66}\text{Zn}_A - \delta^{66}\text{Zn}_B$$

was first used for C isotopes, and is attractive because it’s meaning is intuitively clear (Shackleton and Pisias, 1984). Unfortunately, this terminology is not currently used within the trace-metal community and changing common notation is difficult. Issues of terminology will undoubtedly become more complicated if mass independent isotope effects are discovered in more trace metals such as Fe.

### 1.2.3 Mass-dependant fractionation

For mass-dependent fractionation processes, the magnitude of  $\delta^{68}\text{Zn}$  should be approximately twice the magnitude of  $\delta^{66}\text{Zn}$  (see Chapter 5 for further discussion). The exact relationship between these two quantities depends on the law that is used to describe isotope fractionation. The commonly used “exponential law” takes the form:

$$R_f = R_i \cdot \left( \frac{m_1}{m_2} \right)^\beta$$

where the ratio of two isotopes after fractionation ( $R_f$ ) is related to the initial ratio of the two isotopes ( $R_i$ ) as a function of the isotopic masses ( $m_1$  and  $m_2$ ) and a fractionation factor ( $\beta$ ). According to the exponential fractionation law, the ratio of  $\delta^{68}\text{Zn}$  to  $\delta^{66}\text{Zn}$  will be 1.985.

## 1.2.4 Correcting for instrumental mass bias

### 1.2.4.1 Using Cu or a Zn double-spike to correct for mass bias

During the analysis of Zn isotopes by MC-ICP-MS, large isotopic fractionations are induced in the spectrometer between sample induction and isotope signal measurement. Several different schemes are available to correct for this mass bias. The simplest involves sample-standard bracketing. Assuming that the magnitude of instrumental mass bias is constant between samples and standards, the measured difference in the isotope ratios will be equal to the actual difference in the isotope ratios.

In practice, small differences in the matrix between samples and standards often leads to changes in instrumental mass bias. Instrumental mass bias must be continuously monitored in order to correct for this effect. For Zn, both Cu normalization and a double-spike method can be used. Cu has only two stable isotopes,  $^{63}\text{Cu}$  (69.2%) and  $^{65}\text{Cu}$  (30.8%). By spiking both samples and standards with Cu, changes in instrumental mass bias can be monitored by looking at changes in the measured  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio. The exponential mass bias fractionation factor ( $\beta$ ) calculated for Cu cannot, however, be directly applied to correct for Zn fractionation (Fig. 3). Instead an empirical relationship between the values of  $\beta$  must be established (Maréchal et al., 1999).

A double-spike can also be used to correct for instrumental mass bias. To do this, all samples are spiked with a known mixture of non-natural Zn isotopes, typically  $^{64}\text{Zn}$  and  $^{67}\text{Zn}$ . By simultaneously collecting data on the abundances of  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ , and  $^{68}\text{Zn}$  it is possible to calculate both the concentration ratio of spike to sample and the

mass bias of the instrument. It is then possible to calculate the isotope composition of the original sample.

#### **1.2.4.2 The comparative advantages of Cu and Zn double-spike correction**

Correction with a Cu spike and a Zn double-spike each have their own advantages and disadvantages. A drawback of the Cu correction scheme is that Cu and Zn behave differently during ICP-MS analysis. This is apparent from the fact that values of  $\beta$  are different for these two elements. While the Cu-correction scheme outlined above has been rigorously tested and demonstrated to work well for standards under many conditions (Archer and Vance, 2004; Maréchal et al., 1999), it cannot be proved that this correction scheme always works for real samples.

Another difference is that the Cu correction scheme requires complete recovery of Zn from the sample. Conversely, a Zn double-spike can be added to the sample before processing to account for fractionation of the isotopes during sample processing. This simplifies sample processing, especially in cases such as the analysis of Zn isotopes in seawater where achieving complete recovery of Zn can be difficult.

Finally, the correction schemes differ in that only Cu-correction allows a check for the presence of isobaric interferences by simultaneously measuring  $\delta^{68}\text{Zn}$  and  $\delta^{66}\text{Zn}$ . Isobaric interferences will interfere differently with the measured values of  $\delta^{66}\text{Zn}$  and  $\delta^{68}\text{Zn}$ , causing them to fall off the expected linear relationship governed by mass-dependant fractionation. In double-spike analysis,  $\delta^{66}\text{Zn}$  and  $\delta^{68}\text{Zn}$  cannot be measured simultaneously, so isobaric interferences cannot be distinguished from changes in sample

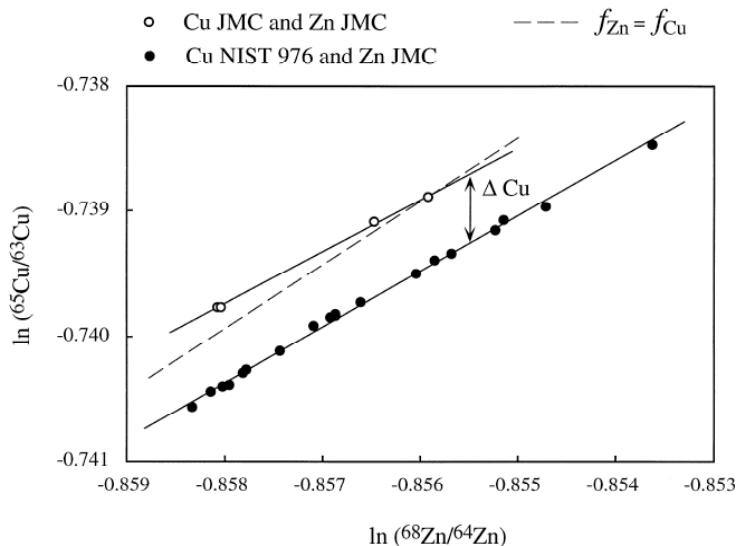


Figure 1.3. During the course of a day, the measured isotope ratios change as instrumental mass bias ( $\beta$ , or  $f$  in this figure) changes. However, the extent of fractionation of these two elements is not the same for the two elements as predicted by the exponential fractionation law. In the case shown here, for example, the exponential mass bias factor for Zn varies by more than the exponential mass bias factor for Cu ( $f_{\text{Zn}} > f_{\text{Cu}}$ ). An empirically determined relationship between  $f_{\text{Zn}}$  and  $f_{\text{Cu}}$  allows one to make a proper correction for varying instrumental mass bias. (Maréchal et al., 1999).

fractionation or instrumental mass bias. Polyatomic isobaric interferences may occur when sample matrix is not completely eliminated. Polyatomic interferences are of special concern on the IsoProbe where an Al sampling cone (rather than Ni) is required for proper heat dissipation. An  $^{27}\text{Al}^{40}\text{Ar}^+$  interference on mass 67 is present with typical signals of several mV.

During data collection for this thesis, a Cu-correction scheme was most often used. A double-spike was used to measure Zn isotopes in six hydrothermal samples (Chapter 3) and several standards. Both correction schemes produced the same results, though the internal error for the Zn double-spike analysis was larger. The origin of this

error is not known, but may result from variations in the magnitude of  $^{27}\text{Al}^{40}\text{Ar}$  interferences.

It might be possible to achieve the advantages of the double-spike method, without introducing susceptibility to isobaric interferences, by making measurements in medium or high-resolution mode where interferences can be separated from Zn by mass. This requires a significantly larger samples size in order to produce the same signal intensity.

### **1.3 Thesis chapters**

Chapter 2 presents data on the Zn isotope ratios found in many anthropogenic materials. Laboratory standards were found to be very fractionated (up to several permil) from typical continental material. The more common types of anthropogenic Zn, such as pennies and health products, were found to have similar values of  $\delta^{66}\text{Zn}$  to continental materials. I discuss how this data can be used to estimate the  $\delta^{66}\text{Zn}$  of many anthropogenic Zn sources into the environment and oceans.

Chapter 3 discusses Zn isotope data for hydrothermal vent fluids and chimneys. Fluids  $\delta^{66}\text{Zn}$  values were measured on samples from several different hydrothermal fields in both the Pacific and Atlantic. A relationship was discovered between the temperature of hydrothermal fluids and their Zn isotope composition. Cooler fluids (<250°C) had  $\delta^{66}\text{Zn}$  values that were significantly heavier than basalt or high-temperature fluids leading us to hypothesize that the subsurface precipitation of light Zn sulfides was associated

with fluid cooling. Measurements from fluids and chimney sulfides taken from the same vent allow us to measure the isotope effect for hydrothermal precipitation *in situ*.

In Chapter 4 we present the results from diatom cultures grown at a range of Zn concentrations and analyzed for Zn isotopes. By carefully distinguishing between extracellular Zn and intracellular Zn, we have been able to measure the isotope effects associated with separate high-affinity ( $\Delta^{66}\text{Zn} = -0.2\text{‰}$ ) and low-affinity ( $\Delta^{66}\text{Zn} = -0.8\text{‰}$ ) transport pathways. These are the first experiments to explain transition metal isotope fractionation in terms of the molecular biology of uptake mechanisms. This data provides a means of relating the  $\delta^{66}\text{Zn}$  of seawater to the biological cycling of Zn in the oceans.

Chapter 5 details efforts to measure Zn isotopes in natural seawater and phytoplankton samples. I have developed new methods for the analysis of Zn concentration in seawater, and a new method for the  $\text{Mg}(\text{OH})_2$  co-precipitation of Zn from seawater for isotopic analysis. Analytical problems with seawater isotope analysis are discussed.  $\delta^{66}\text{Zn}$  values for marine plankton tows range from about 0.0‰ to +0.6‰. Analysis of five separate samples of seawater from the deep Pacific yielded an average  $\delta^{66}\text{Zn}$  of  $+0.50 \pm 0.08\text{‰}$ . There appears to be a trend towards lighter Zn values of  $\delta^{66}\text{Zn}$  in surface seawater. This suggests the preferential removal of isotopically heavy Zn from the surface ocean. I hypothesize that adsorption of Zn onto sinking particles is a major pathway for the removal of Zn from the surface oceans.

Chapter 6 briefly explores some fundamental questions about Zn cycling in the ocean, and the factors that control Zn isotope distribution in the oceans.

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