Carbonates

1. Introduction to carbonate and Ni in carbonates
2. Challenges to measuring Ni in carbonate
   1. Separating Ni from Carbonate matrix
   2. Mention sensitivity tests (neeed Ca, Ti, and Fe below certain levels)

General Data Quality:

Our long term reproducibility of double spike corrected, sample standard bracketed NIST SRM 986 is δ60Ni = 0.000±0.052‰ (n=321).

Challenges

Measuring a sample on a multi-collector inductively coupled plasma mass spectrometer requires that the sample be free of impurities (i.e., any other elements or complexes besides the element of interest). Without purification, there may be isobaric interferences or matrix effects which complicate data interpretation and reliability. We determined the maximum acceptable Element/Ni for Ca, Fe, Zn and Ti by doping SRM 986 Ni standard with the interfering elements at Element/Ni between 0.01 and 1. The threshold value is designated as the greatest Element/Ni that results in a δ60Ni value within the long term 2 SD of δ60NiSRM986. For Ca, Fe, Zn, and Ti, the acceptable Element/Ni were 1, 0.1, 1, and 1 respectively. These data provided clear, quantitative goals for developing our chemical separation plan.

Separating Ni from the carbonate matrix has proved to be a technical challenge (alvarez paper?). The first obstacle is removing the abundance of Ca; the Ca/Ni of the Bahama carbonate samples were approximately 4x105. Next, residual interfering transition metals such as Fe, Zn, and Ti, which may be in equivalent or greater abundance than Ni, must be removed. Finally, if Fe is not yet adequately purified (as determined by the sensitivity tests), an additional purification step should be performed.

To remove Ca and other common seawater constituents (*e.g.,* Mg, Na), we dissolved a generic sample of calcite, aliquoted the amount we would need for isotopic analysis based on the estimated Ni content in the Bahama samples and spiked it with Ni for column tests. We first tested a method from Strelow et al., 1972 which used oxalic acid-hydrochloric acid mixtures and AG1-X8 anion resin in chloride form (Strelow et al., 1972). Elements like Ca do not sorb on the resin in any oxalic-hydrochloric mixture while Ni sorbs at very low hydrochloric acid molarities (ca. 0.1 M) and 0.05 M oxalic acid. However, the insolubility of certain oxalate complexes, such as Ca oxalates, resulted in white precipitates forming which interfered with the column’s efficiency. Ultimately, the final Ni fraction had a Ca/Ni of approximately 7900 and a Ni recovery of <50% which indicates the sample will not be rid of matrix effects or have enough Ni for the double spike technique.

Next, we attempted an augmented version of the methods within Gall et al., 2012 and Strelow, 1990 (Gall et al., 2012; Strelow, 1990) to remove Ca. By combing excess ammonia with ammonium citrate on cation AG50W-X8 resin, Ni binds to ammonia and sorbs to the resin while Ca elutes as a citrate complex. Then, Ni can be easily eluted with 3 M hydrochloric acid. Again, white precipitates, which may have been Ca citrate precipitates, formed when less than 60 mL of loading solution was added to the sample. With this method, we achieved a 85% Ni recovery and final Ca/Ni of ~0.5. This method also removed some transition metals such as Ti, Fe and, V. Unfortunately, the large initial loading requirement would pose two issues. First, using such a large amount of solution increases the amount of Ni contamination. Second, the costly >60 mL Teflon containers needed to handle the samples would slow throughput because purchasing the appropriate number of containers is financially challenging.

We looked to a third method which would ideally remove the issues mentioned above, but still achieve the >70% Ni recovery and Ca/Ni <1. Yang et al., 2020 published a novel method to purify Ni from seawater using a lesser-known resin, NOBIAS-PA1 resin, and ammonium acetate (Yang et al., 2020). They were able to effectively remove >99% of Ca, Na, Mg, and S and had a Ni recovery of >99%. Using this method, we were able to effectively remove Ca to a Ca/Ni of ~0.4 and had a Ni recovery of >98% with only 10 mL of starting solution. We decided to use this column chromatography for the bulk Ca removal step.

The next challenge was to remove the residual interfering transition metals such as Zn, Ti, and Fe. For these tests, we created a trace metal solution which resemble the anticipated trace metal composition of the Bahama carbonate samples using ICP solutions and the Ca concentration after the NOBIAS column. The method described by Gall et al., 2012 and Strelow, 1990 was able to reduce the Ti/Ni, V/Ni and Fe/Ni from 3, 2.5, and 15 to 1, 0.02, and 0.4, respectively. The Ni recovery was >95%. The method did not remove any Zn, which effectively behaved exactly as Ni on the column. We found that, after the bulk Ca removal, there were no white precipitates in 3 mL of loading solution. We decided to use this method to remove most transition metals.

Finally, we needed to remove Zn and residual Fe. To do this, we used a common column for Ni-Fe separation which uses AG1-X8 anion resin and (>6M) hydrochloric acid (Gall et al., 2012; Wasylenki et al., 2015). Iron and Zn form negatively charged chloride complexes which sorb to the resin, while Ni elutes(Kraus and Moore, 1953). Our tests showed this method was able to reduce Fe/Ni and Zn/Ni from 4.5 and 2.5 to 0.01 and 0.3, respectively. The combination of these three columns appears to be adequate to effectively purify Ni from a carbonate matrix (see table XXX for full method).

Ni AAS standard processed through the entire method has a δ60Ni = -0.43±0.05‰ (n=21) which is analytically indistinguishable from the unprocessed Ni AAS standard δ60Ni = -0.44±0.07‰ (n=16).









