# Chromatographic extraction of Fe from seawater and its impact on Fe isotope fractionation

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The recent surge of interest in the isotopic composition of transition metals in natural samples has prompted new research into the development of analytical techniques for their purification. In this study we have examined the application of extraction chromatographic and anion exchange methods to the isolation of transition metals from complex matrices, with particular emphasis on Fe in seawater samples. The precise analysis of transition-metal isotopic composition in natural samples poses two requirements on the chemical purification method: (1) In order to avoid molecular interferences during analysis, all interfering species need to be fully removed, and (2) artificial fractionation during the sample preparation must be ruled out, unless a double-spike method is emplaoyed. The chemical separation of Fe, Cu, Zn and Mo is typically achieved by anion exchange chromatography. This will, however, introduce considerable fractionation unless a 100% yield during chemical processing is achieved. Di-isobutyl-ketone (DIBK) and FerroZine® have been employed in this study as Fe-specific complexants. These were adsorbed onto an Amberlite XAD-7 or C-18 resin respectively to facilitate column chromatographic extraction of Fe. 8-Hydroxyquinoline, which is bonded to Fractogel® EMD Epoxy resin, is used for the purification of a range of trace metals. Elution experiments for these three chromatographic techniques show a markedly reduced isotopic fractionation during the extraction. The performance characteristics of these different methods is reported. Based on these findings we introduce a method for the purification of Fe from seawater sample up to several hundreds of ml in volume.

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# Can Chemical Reactions In The Solar Nebula Produce Anomalous O-Isotope Effects In Silicates And Other Solids?

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Chondritic O-isotopic compositions expressed as $\Delta^{17}O$ (=$\delta^{17}O - 0.52 \bullet \delta^{18}O$) range from –25‰ to +7‰, inconsistent with mass-dependent fractionations. One possibility is that this range reflects the heterogeneous accretion of the solar nebula, with parcels of infalling matter differing in mean $\Delta^{17}O$ (Wasson, 2000). Another possibility is that nebular gases and solids were homogeneous but differing by >32‰ in $\Delta^{17}O$ (Clayton and Mayeda, 1984). A third possibility is that the nebula was initially homogeneous, and that variations in $\Delta^{17}O$ were produced by kinetic or self-shielding processes (Thiemens, 1996; Clayton, 2002).

Formation of $O_3$ from $O_2$ in the stratosphere and laboratory can produce large anomalies at 140-400 K (Morton et al., 1990; Krankowsky et al., 2000). This fractionation is currently explained by symmetry effects. Thiemens (1996) suggested that ozone-like processes are responsible for the chondritic anomalies. To determine whether kinetics-based fractionations are plausible, we examined several questions. a) What is the temperature dependence of reaction rates? b) What other reactions might be capable of producing and retaining large differences in $\Delta^{17}O$? c) Assuming that the anomalous product is gaseous, what mechanism could trans-fer the effect to solids? Our answers to these questions indi-cate that nebular formation of the anomalies is implausible.

To date only ozone formation is documented to produce large $\delta^{17}O/\delta^{18}O \approx 1$ (slope-1) anomalies. Other atmospheric molecules show much smaller effects or may be linked to ozone. Morton et al. (1990) found that the magnitude of the anomaly decreases with temperature.

Refractory chondrite phases have similar isotopic signatures, roughly in the range $\Delta^{17}O$ = -24±3‰. Even if it were possible to produce a minor gaseous species having $\Delta^{17}O$ 20‰ different from $CO_2$ and $H_2O$, we see no way to produce uniform isotopic signatures in refractory oxides. If the species was SiO, how would its signature get into $MgAlO_4$? Because many metals are monatomic, most O in solids originates in $H_2O$ (e.g., 3 O of 4 in $Mg_2SiO_4$). Such processes would not make solids having uniform compositions. We conclude that O-isotopic anomalies resulted from heterogeneous accretion.

**References:** Clayton R. (2002) Nature **415**, 860; Clayton R. and Mayeda T. (1984) *EPSL.* **67**, 151; Krankowsky D., Lämmerzahl P. and Mauersberger K. (2000) *GRL* **27,** 2593 (2000); Morton J., Barnes J, Schueler B., and Mauersberger K. (1990) *JGR* **95,** 901; Thiemens M. (1996) in *Chondrules and the Protoplanetary Disk,* Cambridge, 107; Wasson J.(2000) *Rev. Geophys.***38**, 491.