NUCLEOSYNTHETIC HETEROGENEITY CONTROLS VANADIUM ISOTOPE VARIATIONS IN BULK CHONDRITES.

S. G. Nielsen[1], K. Righter[2], F. Wu[3], J. D. Owens[3], J. Prytulak[4], K. Burton[5], I. Parkinson[6] and D. Davis[7] [1]NIRVANA laboratories, Woods Hole Oceanographiuc Institution, Woods Hole, MA 02543, USA, snielsen@whoi.edu, [2] NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA, [3] Department of Earth, Ocean and Atmospheric Science and National High Magnet Field Laboratory, Florida State University, Tallahassee, FL, USA, [4]Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK, [5]Department of Earth Science, Durham University, Durham, UK, [6] Scool of Earth Sciences, Bristol University, Bristol, UK, [7]Dept. of Geosciences, Georgia State University, Atlanta, GA, USA

Introduction: The vanadium (V) isotope composition of early solar system materials have been hypothesized to be sensitive to high energy irradiation that originated from the young Sun [1, 2]. Vanadium has two isotopes with masses 50 and 51 that have $^{51}V/^{50}V$ ratio of ~ 410. High energy irradiation produces ^{50}V from various target isotopes of Ti, Cr and Fe [1, 3], which would result in light V isotope compositions (expressed as $\delta^{51}V$ in ‰ = 1000 × (($^{51}V/^{50}V_{sample}$/$^{51}V/^{50}V_{AlfaAesar}$) −1)) relative to a presumably chondritic starting composition. Recently published V isotope data for calcium aluminium inclusions (CAIs) has revealed some very negative values relative to chondrites (by almost -4‰) that were indeed interpreted to reflect irradiation processes despite the fact that the studied CAIs all exhibited significant initial abundances of ^{10}Be, while only a few CAIs displayed light V isotope compositions [4]. It is difficult to relate V isotope variations directly to a singular process because V only possesses two isotopes. Therefore, V isotope variations can principally be produced both mass dependent and independent processes. Mass dependent kinetic stable isotope fractionation is common in CAIs for refractory elements due to partial condensation/evaporation processes [5]. The element strontium (Sr) has an almost identical condensation temperature to V [6] and studies of stable Sr isotope compositions in CAIs reveal both heavy and light values relative to chondrites of several permil. These variations are similar in magnitude to those reported for V isotopes in CAIs [7, 8], which suggests it is possible that some of the V isotope variation in CAIs could be due to kinetic stable isotope fractionation during condensation/evaporation processes.

Because V concentrations in refractory inclusions are generally much higher than the matrix of carbonaceous chondrites [9] it might be expected that V isotope compositions of bulk carbonaceous chondrites be affected by the presence of refractory inclusions. In particular, if it is correct that CAIs exclusively exhibit chondritic or lighter V isotope compositions [4] then it is expected that carbonaceous chondrites with the highest abundances of refractory inclusions also display the lightest V isotope compositions. In addition, ordninary chondrites that contain little or no refractory inclusions should be characterized by systematically heavier V isotope compositions than carbonaceous chondrites.

Here we report V isotope data for 10 carbonaceous and 11 ordinary chondrites in order to test the possible origin of V isotope variations in chondritic meteorites.

Methods: Samples were dissolved as 100mg chips from meteorites free of fusion crusts using double distilled concentrated mineral acids such as HF, HNO_3, HCl. The vanadium was separated from sample matrix using a four-step cation/anion exchange chromatography procedure [10, 11]. Mass spectrometry to measure V isotope ratios was performed using a Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS), housed at the Plasma Mass Spectrometry Facility of the Woods Hole Oceanographic Institution (WHOI). Isotope compositions were calculated using standard-sample bracketing with the Alfa Aesar standard that is defined as $\delta^{51}V = 0$‰. Each unknown sample was interspersed with a pure V reference solution from BDH Chemicals that has now been measured in four different labs with the identical result of $\delta^{51}V = −1.2$‰ [10-13]. The mass spectrometer was operated in a medium resolution mode, which ensured that all significant isobaric interferences in the mass spectrum (48–53 atomic mass units) were resolved from the isotopes of interest: ^{48}Ti, ^{49}Ti, ^{50}V, ^{51}V, ^{52}Cr and ^{53}Cr [14]. We collected ^{51}V using a Faraday cup equipped with a 10^{10} Ω resistor, whereas Faraday cups with conventional 10^{11} Ω resistors were used for all other masses collected. Samples and standards were measured at a concentration of 600-800 ng/ml V, which produced an ion beam of ~2 nA on ^{51}V and ~0.005 nA on ^{50} V. The method consumed about 300 ng V per analysis and an external precision of ~0.15‰ (2sd), which was assessed based on repeat measurements of USGS reference materials AGV-2 and BCR-2 that have also been analyzed in previous studies [10, 15, 16]. All samples were measured multiple times (between 2 and 19 individual measurements). Two samples (CO carbonaceous chondrite DOM 08006 and R chondrite NWA 753) were processed at WHOI, Florida State University and Imperial College London

to obtain an interlab comparison and check for the accuracy of the measurements. All three laboratories obtained the same values within error for each of the two samples. Given that the chemical separation procedures utilized in the three labs differ somewhat, these results show that the measurements are robust and that the chemical separation procedures do not impart any systematic bias.

Results and discussion: We find that chondrites preserve a limited range of V isotope compositions from δ^{51}V = -1.05 to -1.35‰. Although this range only covers values slightly outside of the long-term 2sd reproducibility of individual samples, we observe that different samples of the same meteorite group display very similar values, suggesting that individual parent bodies were likely homogenous with respect to V isotopes. There is no discernible difference between carbonaceous and ordinary chondrites, which implies that refractory inclusions in carbonaceous chondrites do not appear to affect bulk V isotope compositions significantly. One enstatite and one rumuruti chondrite both display V isotope compositions within error of the other main chondrite groups. Given the large difference in bulk meteorite redox for these two meteorite types, we suggest that V isotope compositions of chondrites are not affected by the prevailing redox conditions in the area of the solar system where meteorite parent bodies accreted. Among the samples analyzed here six are L chondrites that range in metamorphic grade from L3.0 to L6. There is no measurable V isotopic variation between these six samples, which implies that parent body metamorphism does not produce any V isotope fractionation. This result is consistent with studies of altered terrestrial rocks that likewise display limited effects on V isotopes [16].

Although the overall V isotope variation in carbonaceous chondrites is only 0.3‰, the average values observed for samples from the CO, CV, CK, CR and CM groups exhibit distinct compositions. The lightest group is CK chondrites. This group has lower abundances of refractory inclusions than any of the other groups investigated here. If refractory inclusions were generally characterized by chondritic or lighter V isotope compositions then CK chondrites would be expected to display some of the heaviest values among carbonaceous chondrites. Instead of refractory inclusions affecting the bulk V isotope composition of carbonaceous chondrites, we observe a strong positive correlation between V isotopes and ^{54}Cr nucleosynthetic isotope anomalies. This correlation suggests that V isotope variations in carbonaceous chondrites are primarily controlled by heterogeneous distribution of nucleosynthetically anomalous phases. Models predicting

the isotopic make-up of ejecta from a range of different supernova explosions have reported that ^{54}Cr/^{52}Cr and ^{51}V/^{50}V isotope ratios should be broadly positively correlated [17], which is consistent with the observed correlation for carbonaceous chondrites. Ordinary, enstatite and rumuruti chondrites as well as Earth and Mars, do not conform to the correlation observed for carbonaceous chondrites. However, this could be due to the possibility that the reservoirs that formed carbonaceous and non-carbonaceous meteorites were physically separated in the early solar system [18].

References:
[1] Lee, T., et al., Astrophys. J., 1998. 506(2): p. 898-912.
[2] Burnett, D.S., W.A. Fowler, and F. Hoyle, Geochim. Cosmochim. Acta., 1965. 29(12): p. 1209-1241. [3] Gounelle, M., et al., Astrophys. J., 2001. 548(2): p. 1051-1070. [4] Sossi, P.A., et al., Nature Astronomy, 2017. 1: p. 0055. [5] Simon, J.I., et al., Earth Planet. Sci. Lett., 2017. 472: p. 277-288. [6] Lodders, K., Astrophys. J., 2003. 591: p. 1220-1247. [7] Charlier, B., F.L.H. Tissot, and N. Dauphas, *Goldschmidt*2017: Paris. [8] Charlier, B.L.A., et al., Earth Planet. Sci. Lett., 2012. 329: p. 31-40. [9] Sylvester, P.J., L. Grossman, and G.J. MacPherson, Geochim. Cosmochim. Acta., 1992. 56(3): p. 1343-1363. [10] Wu, F., et al., Chem. Geol., 2016. 421: p. 17-25. [11] Nielsen, S.G., J. Prytulak, and A.N. Halliday, Geostand. Geoanal. Res., 2011. 35(3): p. 293-306. [12] Prytulak, J., et al., Geochemical Perspectives Letters, 2017. 3(0): p. 75-84. [13] Schuth, S., et al., Ore Geol Rev, 2017. 81: p. 1271-1286. [14] Nielsen, S.G., J.D. Owens, and T.J. Horner, J. Anal. At. Spectrom., 2016. 31: p. 531-536. [15] Prytulak, J., S.G. Nielsen, and A.N. Halliday, Geostand. Geoanal. Res., 2011. 35(3): p. 307-318. [16] Prytulak, J., et al., Earth Planet. Sci. Lett., 2013. 365: p. 177-189. [17] Woosley, S.E., A. Heger, and T.A. Weaver, Rev Mod Phys, 2002. 74(4): p. 1015-1071. [18] Warren, P.H., Earth Planet. Sci. Lett., 2011. 311(1-2): p. 93-100.