Chondrule-matrix complementarity in the Allende CV3 chondrite - a Si isotope perspective. Y. Kadlag[1], M. Tatzel[1], D.A. Frick[2], H. Becker[1], and P. Kühne[1], [1]Institute für Geologische Wissenschaften, Freie Universität Berlin, Malteserstrasse 74-100, 12249 Berlin, Germany (yogita@zedat.fu-berlin.de), [2]Helmholtz-Zentrum Potsdam, GFZ German Research Centre for Geosciences, 14473 Potsdam, Germany.

Introduction: Chondrules and matrix are two major constituents of primitive meteorites, together contributing more than 85 vol.% to most carbonaceous chondrites [1]. Previous experimental and theoretical studies on the origin and evolution of chondrules and matrix triggered a debate on the presence of element and isotope complementarity between chondrules and matrix of carbonaceous chondrites. Arguments for and against complementarity have been exchanged in the recent literature [2- 5].

In order to evaluate chondrule-matrix complementarity in carbonaceous chondrites and to shed a light on the details of chondrule formation processes, simultaneous analyses of *in situ* Si isotope ratios, major- and trace element abundances in chondrules and matrix from the carbonaceous chondrite Allende (CV3) were carried out using a laser ablation split stream method using femtosecond LA coupled with MC-ICP-MS and a quadrupole ICP-MS [6].

Methods: The major and minor element compositions of chondrule and matrix minerals from a thin section (~ 17 x 29 mm) of the Allende meteorite were determined prior to laser ablation using a 'JEOL JXA 8200 Superprobe' electron microprobe at FU Berlin. Chondrules were classified based on their mineralogy and textures. 21 chondrules (four barred olivine chondrules, BOC, fifteen type I and type II porphyritic chondrules, PC, one radial pyroxene chondrule, RPC and one cryptocrystalline chondrule, CC) were selected for analyses of Si isotope ratios and abundances of major and trace elements by femtosecond LA-MC-ICP-MS and a quadrupole ICP-MS using sample standard bracketing. δ^{30}Si of samples were determined against the NBS28 (quartz sand) reference standard. The long-term reproducibility of δ^{30}Si in NBS-28 is 0.23 ‰ (2SD). The in-run drift in δ^{30}Si during NBS28 bracketing is < 0.1 ‰ in most cases. The major and trace element abundances were calibrated against NIST SRM 610 and normalized to 100 wt.% element oxides with typical uncertainties of less than 10% (2 SD) for most elements. The accuracy of major and trace element data and δ^{30}Si was determined by analysis of reference materials with variable matrix compositions such as NIST SRM 610, BHVO-2, ML3B, GOR-132G. In two analytical sessions, we have determined BHVO-2 = -0.32 ± 0.32‰ δ^{30}Si, NIST610 = 0.12 ± 0.25‰ δ^{30}Si, GOR-132G = -0.22 ± 0.01‰ δ^{30}Si, ML3B = -0.39 ± 0.23 ‰ δ^{30}Si, in good agreement with literature data [7- 12].

Results and Discussion: The variation of δ^{30}Si and Mg/Fe in chondrules and matrix minerals are summarized in Table 1 and are shown in Fig. 1. The δ^{30}Si of chondrule and matrix silicates show large variation (-1.33 ± 0.15 ‰ to 0.65 ± 0.21 ‰) compared to the Allende bulk rock and CI chondrite value.

Table 1: δ^{30}Si and Mg/Fe data in silicates of chondrules and matrix from Allende. R= refractory element-enriched and V= volatile element-enriched matrix silicates. Bulk rock (BR) values of Allende and CI chondrites are average values from different literature sources [7, 12- 16].

Sample type	δ^{30}Si ± 2SE (‰)	Mg/Fe (±10%)
BOC	0.55 ± 0.20 to -0.38 ± 0.18	1.0-16.9
PC Type I	0.32 ± 0.19 to -0.76 ± 0.12	0.41-18.3
PC Type II	0.24 ± 0.13 to -1.28 ± 0.19	0.25- 5.62
RPC	0.13 ± 0.16 to -0.35 ± 0.16	2.21-10.49
CC	0.14 ± 0.14 to 0.02 ± 0.14	5.3-71.6
Matrix (R)	0.65 ± 0.21	0.46
Matrix (V)	-0.26 ± 0.11 to -1.33 ± 0.15	0.32-0.50
Allende (BR)	-0.45 ± 0.08	0.68
CI chondrites	-0.490 ± 0.15	0.52

The data on chondrules and matrix minerals suggest an increase in δ^{30}Si with Mg/Fe (Fig. 1). Multiple analyses within some individual chondrules also display a positive correlation between δ^{30}Si and Mg/Si. All matrix phases show lower Mg/Fe and ~90% of the matrix silicates show lower δ^{30}Si than the Allende bulk rock and CI chondrites (Fig. 1). All matrix silicates show lower δ^{30}Si than adjacent chondrules. Matrix and chondrule minerals with lower Mg/Fe show a larger scatter of δ^{30}Si compared to the chondrule minerals with higher Mg/Fe. Similar scatter was reported for bulk chondrules (Fig. 1) in a previous study [17]. The δ^{30}Si data show systematic variation with chondrule types (Table 1). The key observations from the variation of δ^{30}Si, Mg/Si and Mg/Fe in chondrules are: silicates in BOC, RPC and CC show higher δ^{30}Si and Mg/Fe than the Allende bulk rock and CI chondrites. Most analyses of type I PC show higher δ^{30}Si and Mg/Fe than CI chondrites and Allende bulk rock. Some analyses on type I and type II PC show lower δ^{30}Si than bulk rocks and CI chondrites. Some analyses (30% in type II PC and 6% in type I PC) show similar Mg/Fe as silicates in matrix, which is lower than the

Mg/Fe of CI chondrites and Allende bulk rock. Based on the systematic variation of δ^{30}Si and Mg/Fe in the chondrule minerals and most of the matrix it appears that either nebular gas or aqueous solutions with enrichment of Fe and isotopically light Si reacted with Mg-rich chondrule cores to form Fe rich rims of type I chondrules and the type II chondrules. The systematic enrichment of Fe and isotopically light Si in matrix and many chondrule rims compared to the chondrule cores favors this scenario.

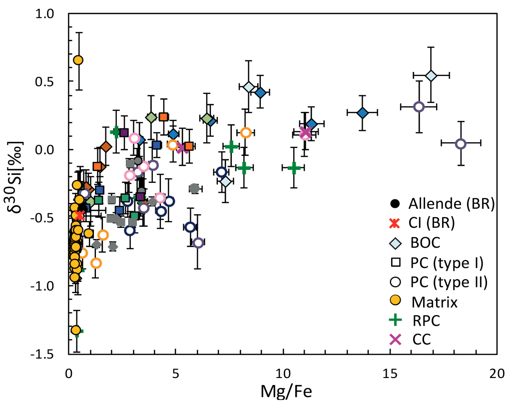

Fig. 1: Mg/Fe vs δ^{30}Si variation in chondrule and matrix silicates. Data shown by gray colored symbols are the bulk chondrule values from [17]

Zoning of Mg/Fe and δ^{30}Si in some chondrules: Textural observations, Mg/Fe, Mg/Si and δ^{30}Si data suggest that the chemical and isotopic variations described above likely reflect a multistep process, which may have taken place in the solar nebula and/or on the Allende meteorite parent body. The significant change in Mg/Fe of most mineral phases of type II PC and some mineral phases of other chondrules likely occurred in the solar nebula, as no corresponding significant change in the Mg/Fe is observed in the adjacent matrix. Evidence from O isotope studies [18] suggests that aqueous alteration on the parent body during hydrothermal metamorphism likely resulted in local formation of Fe-rich olivine-pyroxene veins in chondrules and matrix and may have altered the outer chondrule rim composition. In contrast, the thick chondrule rims likely formed by interaction of chondrule core like-material with Fe and ^{28}Si enriched gas in the nebula [19, 20]. These compositions were only slightly modified later during parent body metamorphism.

Inter-mineral δ^{30}Si variation in the chondrules: The difference in δ^{30}Si of olivine and pyroxene (with similar Fe contents) from two chondrules (BOC and type I PC) is on average ~ 0.75 ‰. The difference in the δ^{30}Si of Fe-rich and Mg-rich olivine compositions are varying from 0.3 to 0.9 ‰ in different chondrules. High temperature equilibrium fractionation between olivine and pyroxene shows only a small difference (<0.1 ‰) in δ^{30}Si [21, 22]. Therefore, the inter-mineral variation of the δ^{30}Si in chondrules cannot be the result of equilibrium isotope fractionation, which also suggests that the chondrule minerals were not in isotopic equilibrium after their formation.

Rayleigh fractionation during open system evaporation of chondrule minerals would lead to a stronger enrichment of ^{30}Si in all chondrule minerals (~11 ‰ for 50% evaporation of Si), which is also not observed. Hence, the variation of δ^{30}Si in the chondrules and matrix is not a direct consequence of single stage equilibrium or kinetic fractionation. Interaction of crystallizing chondrule minerals with gas at elevated pressures may explain these variations.

Conclusion: Significant heterogeneity in δ^{30}Si is observed in chondrules and matrix minerals from the Allende meteorite. Complementary Mg/Fe and δ^{30}Si in most chondrule and matrix silicates support the proposed chondrule-matrix complementarity in CV chondrites. The formation of type II chondrules may reflect interaction of type I chondrules with nebular gas of matrix-like composition.

Acknowledgements: This work and M. Tatzel's fellowship were funded by DFG (SFB-TRR 170 "Late accretion onto terrestrial planets") and FUB. D.A. Frick was supported by the Marie Curie initial training network IsoNose (FP7/2007-2013/grant#608069).

References: [1] Scott and Krot (2007) *Treatise on Geochem., 1,* 1–72. [2] Bland et al., (2005) *PNAS, 102,* 13755–13760. [3] Hezel and Palme (2010) *Earth & Planet. Sci. Lett., 294,* 85-93. [4] Budde et al., (2016) *PNAS, 113,* 2886–2891. [5] Olsen et al., (2016) *Geochim. et Cosmochim. Acta*, *191*, 118-138. [6] Frick et al., (2016) *Analytica Chim. Acta*, *938*, 33-43. [7] Armytage et al., (2011) *Geochim. Cosmochim. Acta 75*, 3662–3676. [8] Savage et al., (2010) *Earth Planet. Sci. Lett. 295*, 139–146. [9] Zambardi and Poitrasson (2011) *Geostand. Geoanal. Res. 35*, 89-99. [10] Fitoussi et al., (2009) *Earth Planet. Sci. Lett. 287*, 77–85. [11] Chakrabarti and Jacobson (2010) *Geochim. et Cosmochim. Acta*, *74*, 6921-6933. [12] George et al., (2007) *Nature 447*, 1102–1106. [13] Savage and Moynier (2013) *Earth Planet. Sci. Lett. 361*, 487–496. [14] Pringle et al., (2014) *Proc. Natl Acad. Sci. USA 111*, 17029-17032. [15] Lodders, (2003) *The Astrophy. J. 591*, 1220-1247 [16] Jarosewich et al., (1987) *Smith. Contr. to the Earth Sci. 27*, 1-49. [17] Armytage (2011) *PhD thesis*, Oxford University, UK. [18] Jabeen et al., (2018) *Met. and Planet. Sci*, https://doi.org/10.1111/maps.13219. [19] Metzler et al., (1994) *Geochim. et Cosmochim. Acta*, *56*, 2873-2897. [20] Morfill et al., (1998) *Icarus 134*, 180-184. [21] Méheut et al., (2009) *Chem. Geol. 258*, 28-37. [22] Qin et al., (2016) *Contrib. Mineral Petrol* 171:91.