

MAGNESIUM, SILICON AND CALCIUM ISOTOPES IN CENTRAL EUROPEAN TEKTITES – IMPLICATIONS FOR HIGH-TEMPERATURE PROCESSES AND TRACKING THEIR SOURCES WITH THE RIES AREA SEDIMENTS. T. Magna¹, J. Farkaš¹, Z. Rodovská^{1,2}, J. Trubač¹, R.B. Georg³, C. Holmden⁴, K. Žák⁵, ¹Czech Geological Survey, Prague, Czech Republic. E-mail: tomas.magna@geology.cz. ²Faculty of Science, Charles University in Prague, Czech Republic. ³Water Quality Centre, Trent University, Peterborough, Canada. ⁴University of Saskatchewan, Saskatoon, Canada. ⁵Institute of Geology, v.v.i., Academy of Science of the Czech Republic, Prague, Czech Republic.

Introduction: Isotopes of Mg and Ca appear to be sensitive indicators of protolith chemistry considering variations of their isotope abundances in silicate and carbonate lithologies [1–2] although Ca as well as Si isotopes may also indicate biologically mediated processes [3]. However, a handful of studies exists that deals with isotope fractionation of these major elements at magmatic temperatures (see review by [4] for Si) and extreme events like impact processes remain largely unexplored [5]. At then-achievable analytical precision, [6] did not discover measurable Mg isotope offsets in tektites from common silicate reservoirs and implied limited loss of Mg that could impart Mg isotope fractionation during impact events. Silicon isotopes are thought to fractionate during core segregation [7] but the response to extreme temperatures remains unknown although it could bear new information on conditions taking place shortly after the giant collisions. Because specific isotope fractionations exist between the vegetation and soils, and due to the fact that some organic materials have been embedded in impact-related glasses [8] and that a minor contribution of ashes from local vegetation into impact-related materials cannot be excluded [9], the high-precision analyses could provide a fingerprint for determining the former presence of flora at impact sites.

Impacts are major surface-shaping processes in early stages of planetary evolution and despite the decreasing rate of large impacts throughout the history, the Earth's surface has constantly been reworked by small to large impacts in its modern era. During the bombardment, natural silica-rich glasses are produced both within the craters and around them, and also as distal ejecta (tektites). Tektites have been recognized in four known strewn fields, which could be assigned to a specific crater or at least the area of origin: North American, Central European, Ivory Coast and Australasian. However, a direct link to their respective protoliths is unclear.

For this study, we selected a range of Central European tektites (moldavites) with distinctive SiO₂ contents and collected from five different strewn subfields in order to cover both the maximum range in chemistry of moldavite and the range in ballistic transport trajectories. In addition, chemically variable Miocene sedi-

ments (mainly the Upper Freshwater Molasse) from the Ries target area in south-eastern Germany (centered close to Nördlingen) that could have contributed to the finite moldavite melt pool were also analyzed. On the basis of the correspondence of the ages [10], the Ries impact structure has been accepted as the parent crater to moldavites.

Results and discussion:

Magnesium. Sediments from the Ries area span a $\delta^{26/24}\text{Mg}_{\text{DSM3}}$ range of $>3\text{‰}$ (–3.0 to 0.1‰) with two distinct trends, apparently related to major element chemistry (MgO, FeO^{tot}) and volatile contents (F, P₂O₅, H₂O). This suggests major lithological contrasts determining the Mg isotope fractionation (carbonate-versus clay- versus quartz-rich sediments) although clay minerals isolated from three sediments do not show a uniform sense of Mg isotope fractionation relative to bulk sediments. Overall, carbonate-rich samples tend towards significantly lower $\delta^{26/24}\text{Mg}$ values than silicate-rich samples. The moldavites span a significantly more constrained range of $\delta^{26/24}\text{Mg}$ values (–1.6 to 0.4‰) and no particular difference is found for moldavites from distinct strewn subfields. The $\delta^{26/24}\text{Mg}$ values overlap with most of the sediments although for the isotopically heaviest moldavite no sedimentary equivalent with similarly heavy Mg isotope composition has been found in this study. These findings may reflect either incomplete sampling of sedimentary precursors or a minor Mg isotope fractionation related to modest Mg loss during the impact event. But with respect to extremely variable Mg contents in the source sediments, any Mg loss during moldavite formation cannot be tested. While both the moldavites and sediments follow mass-dependent isotope fractionation in triple-Mg isotope plot, subtle differences between equilibrium (slope ~ 0.529) and kinetic (slope ~ 0.511) effects are recognized that may be related to low-temperature versus high-temperature conditions. A single sample of a residual glass produced in a power plant during combustion of organic matter (“straw glass”) has a common Mg isotope composition but low Mg content largely precluding significant organic component in the source of moldavites.

Silicon. The $\delta^{30}\text{Si}_{\text{NBS28}}$ values vary greatly for the Ries area sediments (−1.4 to 0.3‰) but no particular difference is observed for silica-rich versus silica-poor samples. A straw glass and phytolith samples isolated from *Miscanthus sp.* carry isotopically heavy Si signature while phytoliths from *Equisetum sp.* carry $\delta^{30}\text{Si}$ at the lower range of values reported for sediments in this study. However, the cumulative effect of plants on the bulk Si systematics is rendered insignificant given the Si-rich nature of target lithologies. Moldavites show more homogeneous $\delta^{30}\text{Si}$ values (−0.5 to −0.1‰) with no difference between the individual strewn subfields. Two moldavites show a systematic and reproducible mass-independent offset in $\delta^{30}\text{Si}$ fractionation (with a slope of ~ 0.56), the origin of which remains presently unclear, but does not appear to be related to peculiar sample chemistry and/or analytical procedures. A slightly wider scatter among the moldavite Si data does not allow to distinguish between different fractionation paths.

Calcium. Contrary to Mg, Ca isotopes are largely invariant in sedimentary samples from the Ries area, with $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$ values ranging between 0.58 and 0.85‰. Two separate positive trends emerge in relation to the carbonate content. A sample of straw glass has a distinctly low $\delta^{44/40}\text{Ca}$ of −0.4‰ which implies a very limited contribution of Ca from vegetation in the moldavites (see the data below). Also, given the low Ca and Mg contents in plants coupled with high Ca/Mg (Ca/Mg in tektites is ~ 1), significant proportion of ashes (several tens percent by volume) would be required to provide detectable changes to Ca–Mg isotope compositions while these amounts would violate other major element constraints. The moldavites display a limited range in $\delta^{44/40}\text{Ca}$ values (0.60 to 0.83‰), within the isotope variability of sediments. Slight differences exist between the different strewn subfields of the Central European moldavites, with the Moravian moldavites having lighter Ca isotope compositions compared with the rest of the suite. Unlike sediments, moldavites do not form a dichotomy but are displaced between low-CaO sedimentary components with the end member $\delta^{44/40}\text{Ca}$ values, i.e., carbonate-rich sediments represent only a marginal addition to moldavite melts.

Several observations can be inferred from the cumulative Mg–Si–Ca isotope dataset. The order of decreasing half-mass condensation temperatures [11] is from Ca to Mg to Si. Calcium shows the highest degree of homogeneity ($\sim 0.06\text{‰/amu}$) in moldavites while both Si and, in particular, Mg display a higher extent of variability ($\sim 0.23\text{‰/amu}$ and $\sim 1.0\text{‰/amu}$, respectively). Therefore, larger degree of variability

discovered for Mg may be, to a certain extent, surprising but this may perhaps be explained by the large range in $\delta^{26/24}\text{Mg}$ values in the possible sedimentary parentage, compared with that found for Si.

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