

## High precision Ca isotope analysis using MC-ICPMS and TIMS

M. SCHILLER\*, C. PATON AND M. BIZZARRO

Centre for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen, DK-1350 Copenhagen, Denmark  
(\*correspondence: schiller@snm.ku.dk)

Calcium is a refractory lithophile element and a major rock-forming constituent of rocky planets. Whereas most Ca isotopes are synthesized during hydrostatic and explosive nucleosynthesis in massive stars, the synthesis of  $^{48}\text{Ca}$  is unique, as it is only efficiently produced in a low entropy environment most likely achieved in a type-Ia supernova [1]. Thus, high-precision Ca isotope measurements of meteorites and their components allow for a better understanding of the nature of the various stellar sources that contributed matter to the nascent solar system.

However, there are several challenges for the precise measurement of Ca isotopes. The natural abundance of the six stable isotopes (40, 42, 43, 44, 46 and 48) of Ca varies by a factor of >24000 (40 to 46), providing an obstacle for the simultaneous measurement of all Ca isotopes. In addition, there is a 20% mass difference between  $^{40}\text{Ca}$  and  $^{48}\text{Ca}$ , which produces a large mass dispersion beyond the geometry of either of the mass spectrometers used in our study. To overcome these issues we used a combination of TIMS and MC-ICPMS, where the low mass range (40-44) was measured using a Triton TIMS, while the overlapping high mass range (42-48) was measured using a Neptune MC-ICPMS. To precisely analyse  $^{46}\text{Ca}$  using the MC-ICPMS we measured in high-resolution ( $m/\Delta m \sim 6500$ ) and at total beam intensities of >5000 V. To further avoid direct isobaric interferences from Ti and Sr, we also established an improved chemical separation of Ca effectively eliminating especially Ti and Sr.

Repeated analyses of rock standards relative to the NIST SRM915b Ca-standard demonstrate that our approach allows the measurement of  $^{40}\text{Ca}/^{44}\text{Ca}$ ,  $^{43}\text{Ca}/^{44}\text{Ca}$ ,  $^{46}\text{Ca}/^{44}\text{Ca}$  and  $^{48}\text{Ca}/^{44}\text{Ca}$  to 50, 2.5, 50 and 12 ppm (2 sd), respectively, when normalized to  $^{42}\text{Ca}/^{44}\text{Ca}$ . This represents a 100-fold improvement compared to previous studies for the less abundant isotopes of Ca. Using this improved resolution, we have re-investigated the extent of Ca-isotope heterogeneity in the solar protoplanetary disk by analyzing a suite of strategically-selected inner solar system objects.

[1] Meyer (1998) *Phys. Rep.* **227**, 257–267.

## Inhibition of calcite dissolution kinetics during direct liming of acid surface waters

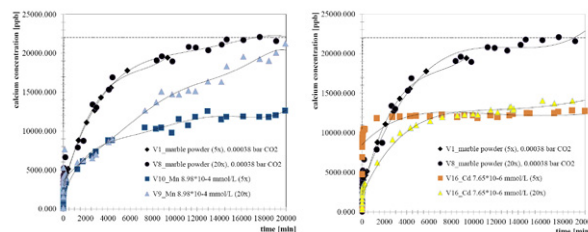
M. SCHIPEK\* AND B.J. MERKEL

TU Bergakademie Freiberg, Chair of Hydrogeology, 09596 Freiberg, Germany  
(\*correspondence: schipek@geo.tu-freiberg.de)

Dissolution kinetics of pure calcite is well investigated, e.g. [1, 2]. But, composition of natural carbonates, as well as the constituents in mine waters, have a strong influence on the solution kinetics and may inhibit dissolution processes during lake liming.

The reactivity of synthetic marble powder and industrial products was investigated. Significant differences in reactivity was obvious at  $p_{\text{CO}_2} > 3.8 \cdot 10^{-4}$  atm. Ions typical for acid mine drainage (e.g.  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{SO}_4^{2-}$ ) do have different effects on the kinetic of carbonate dissolution. Manganese ions ( $c = 8.98 \cdot 10^{-4}$  mmol/L) inhibit calcite dissolution. Experiments with 5-times excess of calcite results in 66.4% of dissolved calcium compared to experiments without inhibitor. Providing a surplus of calcite particles (20-times excess) results in 92.7% of the equilibrium concentration and a significant time-shift in reaching equilibrium (20,000 min instead of 12,000 min).

Cadmium has as well a significant influence on dissolution and kinetics. Only 58.2% of the calcium concentration was reached with cadmium as inhibitor ( $c = 7.65 \cdot 10^{-6}$  mmol/L) compared to the dissolution in pure water. Using carbonate 20 times in excess revealed a slightly higher dissolution reaction (63.8%).



Increased  $\text{CO}_2$  partial pressure might be used to compensate inhibition by material impurities and/or water constituents.

[1] Plummer *et al.* (1978) *American Journal of Science* **278**(2), 179–216. [2] Dreybrodt *et al.* (1996) *Geochim Cosmochim Acta* **60**(18), 3375–3381.