

1.6.P06**The fate of structure-bound Mn²⁺ during the decomposition of dolomite and in the resulting conversion products**A.U. GEHRING¹, P.G. WEIDLER² AND J. GRANWEHR³¹Institute of Geophysics, ETH Zurich, CH-8093 Zurich (gehring@sl.ethz.ch)²Forschungszentrum Karlsruhe, D-76021 Karlsruhe (peter.weidler@itc-wgt.fzk.de)³Department of Chemistry, UC Berkeley; Berkeley, CA 94720, U.S.A. (joga@waugh.cchem.berkeley.edu)

Dolomite often contains impurities (e.g. structure-bound trace elements), which can influence its reactivity. Little is known about the fate of these impurities during the thermal conversion into lime (CaO) and periclase (MgO). The substitution of Ca²⁺ and Mg²⁺ by Mn²⁺ is a classical example for such an impurity.

The Mn²⁺ substitution in synthetic and natural dolomite has been characterized in several studies by continuous wave (cw) electron paramagnetic resonance (EPR) spectroscopy, and EPR parameters like the electron **g** matrix, the hyperfine splitting (HFS) tensor **A** or the zero-field splitting (ZFS) tensor **D** are available for Mn²⁺ in Ca- and Mg-sites of dolomite. The separation of the two sites is only possible if the Mn²⁺ concentration is low and the paramagnetic centers are highly diluted in a diamagnetic matrix, such that they can be considered as isolated from each other.

Dolomite from Jhamarkotra phosphate mine (India) contains 680 ppm Mn in its divalent form as indicated by EPR. Dipolar broadening of the cw EPR signal prevents a quantitative assignment of Mn²⁺ to Ca- and Mg-sites. Upon heating to 700°C over 99% of dolomite is decomposed and all Mn²⁺ is released from the dolomite structure. 95% of the original Mn²⁺ is oxidized and forms Mn-oxide, which is not EPR detectable.

The remaining Mn²⁺ preferentially migrates into CaO as indicated by cw and two-pulse echo detected EPR analysis. This behavior is interpreted by the Goldschmidt rule stating that smaller ions are taken up in sites of larger ions.

During subsequent hydration of CaO into Ca(OH)₂, Mn²⁺ remains stable. The protection of Mn²⁺ against oxidation is explained by the topotaxial alteration of the host minerals, where the oxygen layers of CaO[111] are parallel the hydroxyl layers of Ca(OH)₂[0001]. Carbonation of the Ca(OH)₂ leads to Mn²⁺ oxidation caused by the dissolution of the hydroxide prior to the formation of CaCO₃.

In summary, divalent Mn monitored by EPR can be used as an example to unravel the behavior of trace elements on the molecular level during mineral alteration.

1.6.P07**Three-dimensional nanoanalysis of a metamorphic magnetite**K.R. KUHLMAN¹ AND T.F. KELLY²¹Jet Propulsion Laboratory, California Institute of Technology, M/S: 302-306, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A. (kkuhlman@jpl.nasa.gov)²Imago Scientific Instruments Corp., 6300 Enterprise Lane, Madison, WI 53719 USA. (tkelly@imago.com)

We have successfully fabricated atom probe samples of a metamorphic magnetite and performed an analysis of one of these samples using a local electrode atom probe (LEAP) [1]. This particular magnetite, previously designated LP204-1, was extracted from a polymetamorphosed, granulite-facies marble and contains grain scale heterogeneity in its oxygen isotope ratios [2]. Crystals of LP204-1 contain a high number density of nanometer-scale, disk-shaped Al-Mn-Fe-spinel precipitates making this magnetite particularly attractive for demonstrating the capabilities of the LEAP with regard to geological materials [3]. Field ion microscope images of these magnetite crystals show precipitate size and morphology that agrees with previous results [4].

A sample of LP204-1 was analyzed in the LEAP, resulting in a cylindrical analyzed volume approx. 26 nm in diameter and 21 nm high. The mass spectrum contained nearly 106,000 atoms, 97.1% of which were identified. Peaks for singly, doubly and triply ionized species were fully resolved. The analysis volume appeared to be purely magnetite. The elemental composition of the analyzed volume is given in Table 1. It appears that the oxygen content is less than that of stoichiometric magnetite (57.1 at%).

Table 1. Elemental composition of LP204-1 as analyzed in the LEAP.

	Atomic Percent
Fe	42.7
O	49.6
Mn	1.6
Al	0.5
Mg	1.3
Total	97.1

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References

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